

and advice. This work was carried out under the Masson Memorial Scholarship awarded to one of them (J. B. W.) by the Australian Chemical Institute.

Summary

1. The polarographic reduction of a number of complexes of cobalt (III) with ammonia and ethylenediamine have been studied in *N* and 0.1 *N* potassium sulfate and in 0.1 *N* sodium acetate.

2. In all cases reduction takes place in two stages, the first involving one, and the second, two, electrons. The half-wave potential of the first step varies from compound to compound, but

that of the second is the same for all compounds. It is considered probable that the first step corresponds to the reduction and disruption of the complex ion to form $\text{Co}(\text{H}_2\text{O})_6^{++}$; the second step corresponding to the reduction of $\text{Co}(\text{H}_2\text{O})_6^{++}$ to cobalt.

3. A correlation is made between the mechanism of reduction proposed and the decomposition processes of the nitro-cobaltamines when adsorbed on charcoal. The relative stabilities of the compounds as shown by the two methods are in fair agreement.

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[CONTRIBUTION FROM THE COATES LABORATORY OF LOUISIANA STATE UNIVERSITY]

The Characterization of Silicic Acid-Celite Mixtures for Chromatography

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In order to use chromatography most effectively, it is necessary to select the best adsorbent for a given purpose. This requires a thorough knowledge of the properties of the materials used.

Several methods have been devised for standardizing adsorbents: the use of dye mixtures by Brockmann and Schodder¹; the calorimetric method of Müller²; the use of V_t (threshold volume) by H. Weil-Malherbe³; and the method suggested by the present author.⁴

It is the purpose of this paper to show that the terms suggested by the author permit a good characterization of adsorbents. For this study the system silicic acid-Celite was selected. The terms evaluated are: S , V_c , R ,⁵ and T_{50} .^{6,7}

These terms can be made more specific by certain notations: the solvent, etc., may be specified: V_c^{benzene} , T_{50}^{benzene} , $R_{p\text{-nitroaniline}}^{\text{benzene}}$. Unless otherwise noted R refers only to the lower edge of a zone, however in some studies it is useful to determine R for both top and bottom edges of a zone, R_t and R_b .

(1) H. Brockmann and H. Schodder, *Ber.*, **74**, 73 (1941).
(2) P. B. Müller, *Helv. Chim. Acta*, **26**, 1945 (1943); **27**, 404, 443 (1944); *Verhandl. Ver. Schweiz. Physiol.*, **21**, 29 (1942).

(3) H. Weil-Malherbe, *J. Chem. Soc.*, 303 (1943).

(4) A. L. LeRosen, *THIS JOURNAL*, **64**, 1905 (1942).

(5) The terms were defined as follows (ref. 4):

S = length of adsorbent column containing one unit volume of solvent/length of unfilled tube required to contain the same volume of solvent.

V_c = rate of flow of the developing solvent through the column when a state of constant flow has been reached (mm./min.).

R = rate of movement of the adsorbate zone (mm./min.)/rate of flow of the developing solvent (V_c).

(6) Suggestion by the author, mentioned first by L. Zechmeister and A. Polgár, *THIS JOURNAL*, **66**, 137 (1944), footnote 10.

(7) T_{50} is defined for used with a 9 mm. dia. tube in place of the 20 mm. dia. tube of ref. 6.

T_{50} = the time in seconds required for a solvent to penetrate 50 mm. into an initially dry $9 \times 75 \approx 2$ mm. column under a vacuum given by the water pump. This term is defined for a specific column due to the lack of sufficient data for columns of other sizes.

In this work a change has been made from the larger (20 × 200 mm.) chromatographic tube previously used to the smaller 9 (inside diameter) × 130 mm. tube. All tests were standardized on a column of adsorbent 75 ± 2 mm. long. The smaller tube requires less adsorbent and is more convenient than the larger one.

Several kinds of silicic acid were tested and the results are given in Table I. The pre-washing

TABLE I

THE CHROMATOGRAPHIC CHARACTERISTICS OF SEVERAL SILICIC ACID SAMPLES

Adsorbent brand	S	T_5	V_c	$R_{p\text{-nitroaniline}}^{\text{benzene}}$ Un- treated	Pre- washed ^a
Merck Reagent (Approx.)					
H_2SiO_3	1.54	121	9.8	0.22	0.031
J. T. Baker, C. P.	1.42	10.5	90.0	0.59	0.520
Central Scientific Company, Tech.	1.65	148.0	6.8	0.85	...

^a See Table II.

TABLE II

THE CHARACTERISTICS OF SILICIC ACID (MERCK)-CELITE MIXTURES^a

Silicic acid fraction in mixture		S	T_{50}	V_c	$R_{p\text{-nitroaniline}}^{\text{benzene}}$ Un- treated	Pre- washed ^b
Wt.	Vol.					
1.00	1.00	1.54	121	9.8	0.22	0.031
0.90	0.83	1.51	69	18.9	.26	.034
.80	.69	1.49	54	22.6	.30	.038
.67	.52	1.45	24	52.0	.34	.050
.50	.36	1.41	12	88.0	.48	.096
.20	.12	1.31	7	165.0	.68	.245
.00	.00	1.24	4	326.0	1.00	1.000

^a Celite (No. 535) is manufactured by the Johns-Manville Co., 22 E. 40th St., New York 16, N. Y.

^b These columns were pre-washed with 3.3 ml. of acetone, 3.3 ml. dry ether, and 6.6 ml. petroleum ether (b. p. 60-70°) to remove moisture. (The removal of moisture is indicated by the presence of droplets of water in the washings from the column. The water was identified positively.)

treatment has been developed by a number of workers, and has been found to increase the strength of an adsorbent in some cases.

Table II gives properties of silicic acid-Celite mixtures; the variation of R with composition is shown in Fig. 1.

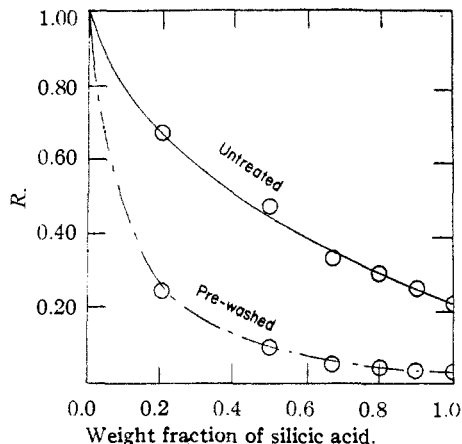


Fig. 1.—Variation of R_p^{benzene} with composition of silicic acid-Celite mixtures.

The values of the individual terms considered most suitable will depend on the nature of the chromatographic problem; however, the following ranges are satisfactory in many cases

$$\begin{aligned} V_c &= 10 \text{ to } 50 \text{ mm. per min.} \\ T_{50} &= 20 \text{ to } 100 \text{ sec.} \\ R &= 0.10 \text{ to } 0.30 \end{aligned}$$

No special requirement seems necessary for S at present.

On the basis of these statements the best adsorbent mixtures may be selected from Table II. The values for T_{50} and V_c apply to both washed and unwashed adsorbent, suitable values are found in the range 67 to 90% silicic acid. A consideration of R now shows that the 80 and 90% mixtures are in the acceptable range for the unwashed adsorbent, while the 67% mixture is best for the pre-washed adsorbent, although the R value is below the limit set. In this case a change of developer may give a suitable value for R .

The term R is a fundamental quantity. The average time a solute molecule spends in solution between each adsorption may be designated T_s and the average time on the adsorbent for each adsorption T_a . The fraction of the total time spent in solution is $T_s/(T_a + T_s)$, and during this period the particle moves down the column with the speed of the solvent, therefore

$$\text{Velocity of zone} = [T_s/(T_a + T_s)] \times (\text{velocity of solvent})$$

The fraction of the total time spent in the solution is identical with R . A linear adsorption equation and R are simply related: $A = k(c)$, where A is the amount of substance adsorbed on the adsorbent in equilibrium with one unit volume

of solution of concentration c . It follows⁸ then that $R = 1/(k + 1)$, and if the amount of adsorbent in a given volume is reduced to a fraction, n , of the original, $R = 1/(nk + 1)$ or $nk = (1 - R)/R$. Figure 2 indicates that the latter relation is linear for the volume fraction of silicic acid in the mixture.

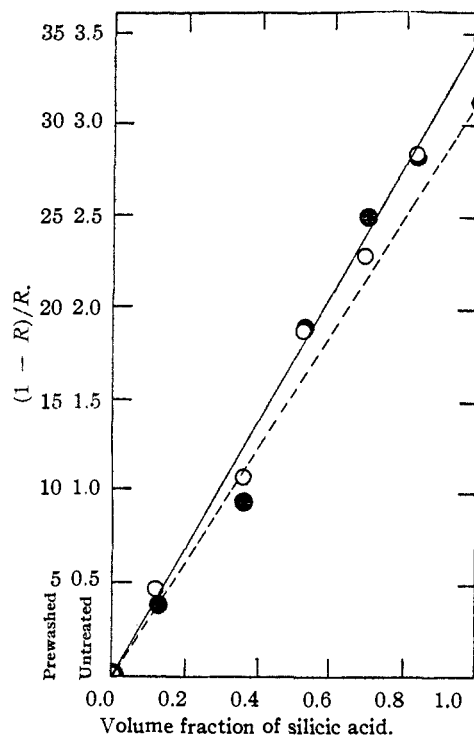


Fig. 2.—Plot of $(1 - R)/R$ against the volume fraction of silicic acid (prewashed, ●; untreated, ○) in silicic acid-Celite mixtures.

The filtration rate under a water pump vacuum is measured by V_c and T_{50} . The reciprocal relation between these two quantities is shown in Fig. 3. When \log_{10} of V_c or T_{50} was plotted against the volume fraction of silicic acid in the mixture a linear relation was obtained. Figure 4 shows this relation. In the case of either V_c or T_{50} the slope of a straight line connecting the values for the pure adsorbent and the filter aid is fixed by these values. If this relation is applicable to other systems of adsorbent-filter aid mixtures it may be quite useful in predicting the filtering

(8) This relation is derived as follows: if a solution of concentration c is poured on a column until the adsorbate zone reaches the boundary of an element of volume, assuming that equilibrium is attained and that simultaneously the solute reaches the boundary at concentration c , the total amount of adsorbed and dissolved solute in the zone is $(k + 1)c$. To introduce this amount of solute the solvent must move through $k + 1$ elements of volume while the zone has moved through 1 element giving the movement ratio, zone/solvent (R); $1/(k + 1)$. For zones that change in width on development this treatment is only approximate, cf. J. N. Wilson, THIS JOURNAL, 62, 1583 (1940); D. DeVault, *ibid.*, 65, 532 (1943); A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, 35, 1358 (1941); J. Weiss, *J. Chem. Soc.*, 297 (1943).

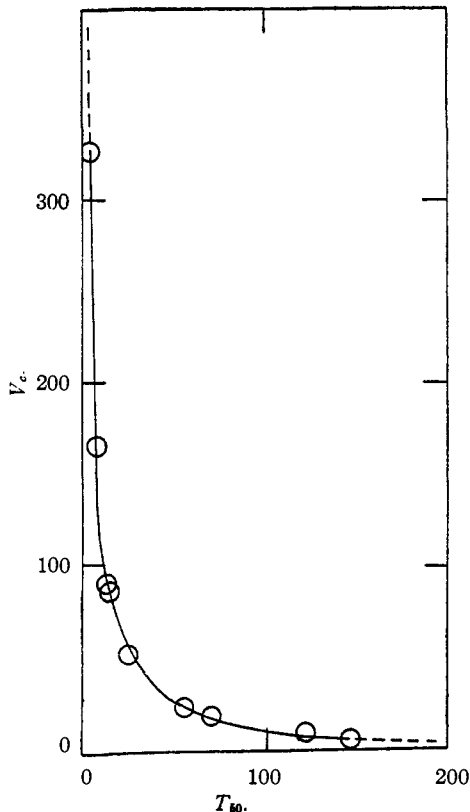


Fig. 3.—Relation between T_{50} and V_c for silicic acid-Celite mixtures.

properties of mixtures from values for the separate materials.

The packing of the adsorbent was found to be a

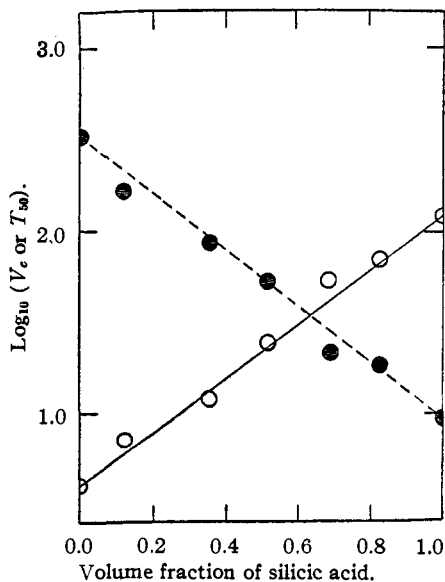


Fig. 4.—Plot of $\log T_{50}$, O, and $\log V_c$, ●, against volume fraction of silicic acid in a silicic acid-Celite mixture.

linear function of the weight composition of the mixture, the variation of S with composition is shown in Figure 5.

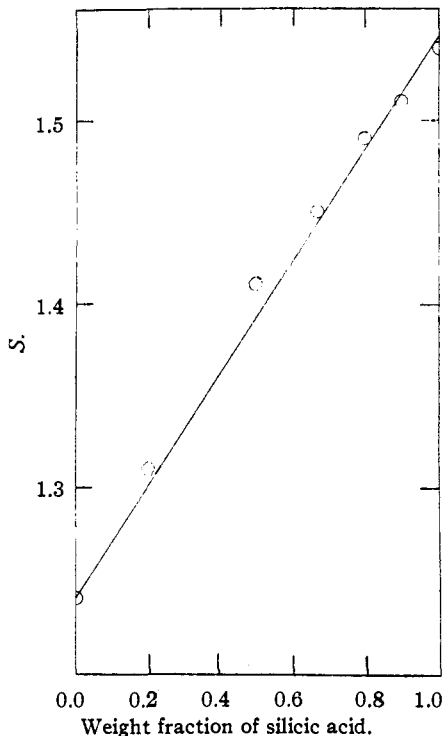


Fig. 5.—The relation between S and the weight fraction of silicic acid in silicic acid-Celite mixtures.

The data are precise to about the following per cent. of the values, $S \pm 2$, $T_{50} \pm 10$, $V_c \pm 10$, $R \pm 10$. Some improvement may be expected with refinement of methods of measurement and apparatus.

Experimental

Materials.—The benzene and petroleum ether used were not specially purified; the acetone was redistilled before use and the ether was dried over sodium wire. The *p*-nitroaniline was introduced into the column as 1 mg. dissolved in 0.2 ml. of benzene.

Apparatus.—The chromatographic tubes (no. 1, 9 (inside diameter) \times 130 mm.) were obtained from the Central Scientific Co., 47 Ackerman St., Bloomfield, New Jersey. All of the diameter values given for tubes refer to the inside diameter.

Determination of S , V_c , and R .—The determination of these characteristics has already been described⁴; they were made under the vacuum supplied by a water pump. For these experiments the average driving force was a pressure difference between the ends of the column of about 700–720 mm. Unpublished studies indicate that this corresponds to a 5% uncertainty in V_c . In the present investigation a smaller tube was used, 9 \times 130 mm. It was found that both R and V_c could be measured satisfactorily in the same determination. It is important to note here that columns were packed under vacuum alone, and that settling was aided only by tapping the sides of the tube. No appreciable pressure was exerted on the top of the column in leveling the surface. For substances like Celite the value of filtration constants may be greatly altered by applying pressure to the top of the column in packing.

Determination of T_{50} .—A column of adsorbent 75 \pm 2 mm. long was prepared in a chromatographic tube 9 \times 130 (outside dia. 11 mm.) then solvent (about 2.5 ml.) was introduced and the time required for it to reach a point 50 mm. from the top of the column was measured with a stopwatch. This value was recorded as T_{50} . This measurement can usually be made in the same determination as S .

Summary

Several silicic acid samples and mixtures con-

taining varying proportions of silicic acid and Celite have been evaluated as chromatographic adsorbents using the terms: S , measuring column packing, V_c and T_{50} , measuring rate of solvent flow, and R , measuring adsorption affinity. A linear relation was found between the composition of the mixtures and some function of each of the terms.

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The Derivation of Water Activities from Electromotive Force Data

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Introduction

The partial molar free energies of solvent and solute are connected by the Gibbs-Duhem equation

$$n_1 d\bar{F}_1 = -n_2 d\bar{F}_2$$

which becomes, for aqueous solutions, using the molality scale

$$55.51 d \ln a_w = -m d \ln a_2 \quad (1)$$

a_2 representing the activity of the solute and a_w the water activity. In terms of the osmotic coefficient, $\phi = -(55.51/vm) \ln a_w$, and the stoichiometrical activity coefficient, γ , this leads to the equation of Randall and White¹

$$-\ln \gamma = h + 2 \int_0^m (h/\sqrt{m}) d\sqrt{m} \quad (2)$$

where $h = 1 - \phi$, by means of which water activity data are readily made to yield activity coefficients. The corresponding equation for converting activity coefficients into osmotic coefficients is

$$h = -(1/m) \int_0^m m d \ln \gamma \quad (3)$$

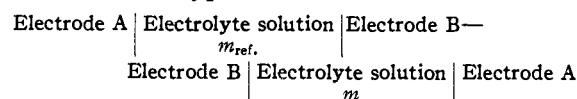
This form is by no means as useful for computational purposes as (2), since the integral forms the whole of the required quantity instead of only a part as in (2). Consequently the graphical integration of m with respect to $\ln \gamma$ must be carried out with great accuracy and is a very time-consuming process. Furthermore, it frequently demands γ values at closer intervals than those experimentally available so that recourse must be had to interpolation formulas. A third disadvantage of equation (3) is that in certain cases where γ is derived from e. m. f. measurements on cells with hydrogen electrodes, the cell reaction involves water. In such cases γ cannot be evaluated without prior knowledge of the water activities and a series of approximations for γ and a_w is necessary until values consistent with (2) and (3) are obtained.

Accordingly the general method now presented, by which water activities may be derived directly

from e. m. f. measurements on cells without transference, should be of interest.

Development of Equations

In a complete concentration cell without transference, of the type



the cell reaction may be represented by: 1 molecule electrolyte at concentration $m + r$ molecules of water in solution of concentration $m_{\text{ref.}}$ \rightarrow 1 molecule electrolyte at concentration $m_{\text{ref.}}$ + r molecules water in solution of concentration m , per n electrons transferred. Here n is the valency of the ion of highest valency present and r is an integer depending on the specific cell used, usually zero, except in certain cells involving hydrogen or metal oxide electrodes.

The free energy change in such a cell is given by

$$-nEF = \bar{F}_2 - \bar{F}_{2\text{ref.}} - r(\bar{F}_w - \bar{F}_{w\text{ref.}}) \quad (4)$$

Differentiating, since $n_{\text{ref.}}$ is constant

$$-nF dE = d\bar{F}_2 - r d\bar{F}_w$$

which by equation (1) becomes

$$\begin{aligned} (nF/RT) dE &= (55.51/m) d \ln a_2 + r d \ln a_w \\ (F/RT) dE &= (55.51 + rm)/nm d \ln a_w \end{aligned}$$

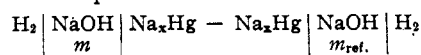
Hence

$$\ln a_w/a_{w\text{ref.}} = (F/RT) \int_{m_{\text{ref.}}}^m nm/(55.51 + rm) dE$$

Defining $m' = nm/(55.51 + rm)$, we have finally

$$\log a_w/a_{w\text{ref.}} = F/(2.303 RT) \int_{m'_{\text{ref.}}}^{m'} m' dE \quad (5)$$

which gives an explicit expression for a_w in terms of the molalities and the electromotive forces. Equation 5 is a generalized form of that used by Åkerlöf and Kegeles² for the evaluation of water transfer potentials for the cell



(1) M. Randall and A. M. White, *THIS JOURNAL*, **48**, 2514 (1926).

(2) G. Åkerlöf and G. Kegeles, *ibid.*, **62**, 620 (1940).