NOTA 799 I   maart 1974

Instituut voor Cultuurtechniek en Waterhuishouding
Wageningen

DESORPTION CURVE EQUATION

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Nota's van het Instituut zijn in principe interne communicatiemiddelen, dus geen officiële publikaties.
Hun inhoud varieert sterk en kan zowel betrekking hebben op een eenvoudige weergave van cijferreeksen, als op een concluderende discussie van onderzoeksresultaten. In de meeste gevallen zullen de conclusies echter van voorlopige aard zijn omdat het onderzoek nog niet is afgesloten.
Bepaalde nota's komen niet voor verspreiding buiten het Instituut in aanmerking.

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ADSORPTION ISOTHERM EQUATION

(D.H. FINK and R.D. JACKSON: Soil Science 116, 4).

The adsorption isotherms of water on most soil and clay material are sigmoidal in shape i.e. Type II classification (BRUNAUER et al., 1940). A mathematical expression sigmoidal in form that relates the probability distribution of particles to their energy states (HEMENWAY et al., 1967) formed the beginning of our development. The equation is

$$Pr = 1 / \left[1 + \exp(\alpha + \beta \, . \, E)\right] \qquad (1)$$

The parameters Pr and E were empirically related to the relative vapor pressure P/Po and the water content W, respectively, subject to the conditions

$$W \longrightarrow \infty \quad \text{as } P/Po \longrightarrow 1 \qquad (2a)$$

$$W \longrightarrow 0 \quad \text{as } P/Po \longrightarrow 0 \qquad (2b)$$

and

$$d^2W / d\left(\frac{P}{Po}\right)^2 = 0 \qquad (2c)$$

for a single value of P/Po in the range of $0 < P/Po < 1$. Conditions (2a, 2b and 2c) are met by defining $Pr = (P/Po)^c$ and $E = \ln W$, where c is a constant to be determined. Substituting into equation (1) and rearranging yields

$$Pr = 1 / \left[1 + \exp(\alpha + \beta \, . \, E)\right]$$

$$Pr \left[1 + \exp(\alpha + \beta \, . \, E)\right] = 1$$

$$1 + \exp(\alpha + \beta \, . \, E) = 1 / Pr$$

$$\exp(\alpha + \beta \, . \, E) = \frac{1}{Pr} - 1 = \frac{1 - Pr}{Pr}$$

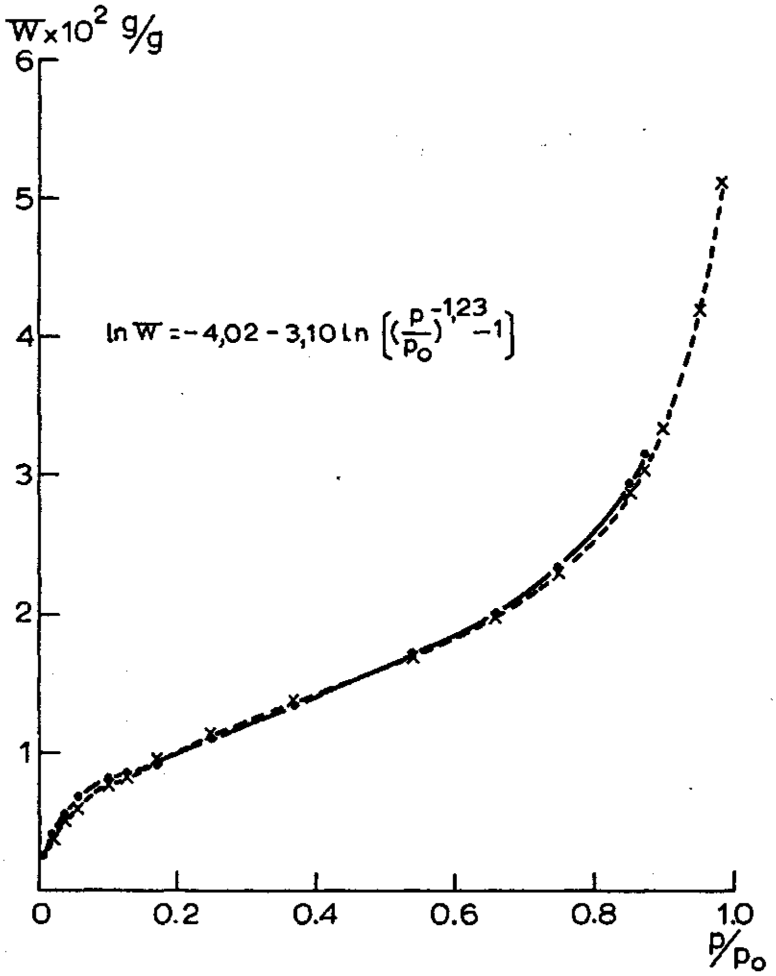

Fig. 1. Adsorption isotherms of water on soil material. Solid line represents experimental data and dashed line is calculated from these data using equation $\ln \overline{W} = A + B \ln \left[(P/P_o)^{-c} - 1 \right]$ (where: A = -4.02, B = -3.10, c = 1.23). The correlation coefficient (r) between the experimental $\overline{W}$ and the calculation $\overline{W}$ using equation is 0.999.
(Data source: CARY et al., 1964. Sample: Milliville loam soil at 24.8°C) (see Table 1)

Table 1. Comparison of the experimental data of adsorption isotherms W and W' calculated by adsorption isotherm equation $\ln W = -4.02 - 3.10 \ln \left[\left(\frac{P}{P_o} \right)^{-1.23} - 1 \right]$.

P : vapor pressure (mm H_2O)
P/P_o : relative vapor pressure (P_o = 318.9 mm H_2O at 24.8°C)
W : water content (mg H_2O/g. soil)

(Data source: CARY et al., 1964. Sample: Milliville loam soil)

P	P/P_o	W	calculated W'
0.2	0.0006	1.07	1.05
2.5	0.007	2.65	2.69
6.9	0.02	4.26	4.03
13.0	0.04	5.64	5.26
21.8	0.06	6.82	6.18
34.1	0.10	8.12	7.53
41.7	0.13	8.47	8.41
55.5	0.17	9.36	9.43
81.6	0.25	11.29	11.21
120.5	0.37	13.50	13.63
172.7	0.54	17.34	17.19
211.1	0.66	20.22	20.20
242.2	0.75	23.75	23.32
271.7	0.85	29.43	28.54
278.5	0.87	31.70	30.08
	0.90		33.02
	0.95		44.73
	0.98		56.08

$$\alpha + \beta E = \ln \frac{1 - Pr}{Pr}$$

$$\beta . E = \ln \frac{1 - Pr}{Pr} - \alpha$$

$$E = \frac{1}{\beta} \ln \left(\frac{1}{Pr} - 1 \right) - \frac{\alpha}{\beta}$$

$$E = \ln W \ , \ Pr = (P/Po)^{c} \ , \ \frac{1}{\beta} = B \ , \ - \frac{\alpha}{\beta} = A$$

$$\ln W = A + B \ln \left[\left(\frac{P}{Po} \right)^{-c} - 1 \right] \qquad (3)$$

where A, B and c are adjustable constants obtained by fitting the equation to experimental data.

Equation (3) is fitted to experimental data by choosing an initial value of c and solving for A, B and the correlation coefficient r by linear regression. Using a simple computer program, the regression procedure is repeated using sequentially stepped values of c until the maximum value of r is obtained for the particular set of adsorption data, with c determined to three significant figures.

The constants A, B and c of equation (3) along with the corresponding r values were computed for a published set of data on water absorption on soils.

One of these examples is shown in Fig. 1 and Table 1 (original data: CARY et al., 1964). The data for Milliville loam soil at 24.8°C indicate excellent agreement between calculated and measured as shown in Fig. 1.

The temperature appears in this note because it makes use of the data of CARY et al. (1964). The temperature is in his paper of importance because he measures the amount of absorbent at relative pressure P/Po, whilst the changes in the absorption isotherms of the Milliville loam is caused by changes in vapour pressure and not by negative moisture pressure as in this note. Therefore the temperature has only a slight meaning on the following pages and will be left out of the discussion of the results of the determination of the pF-curve for the Salland soils.

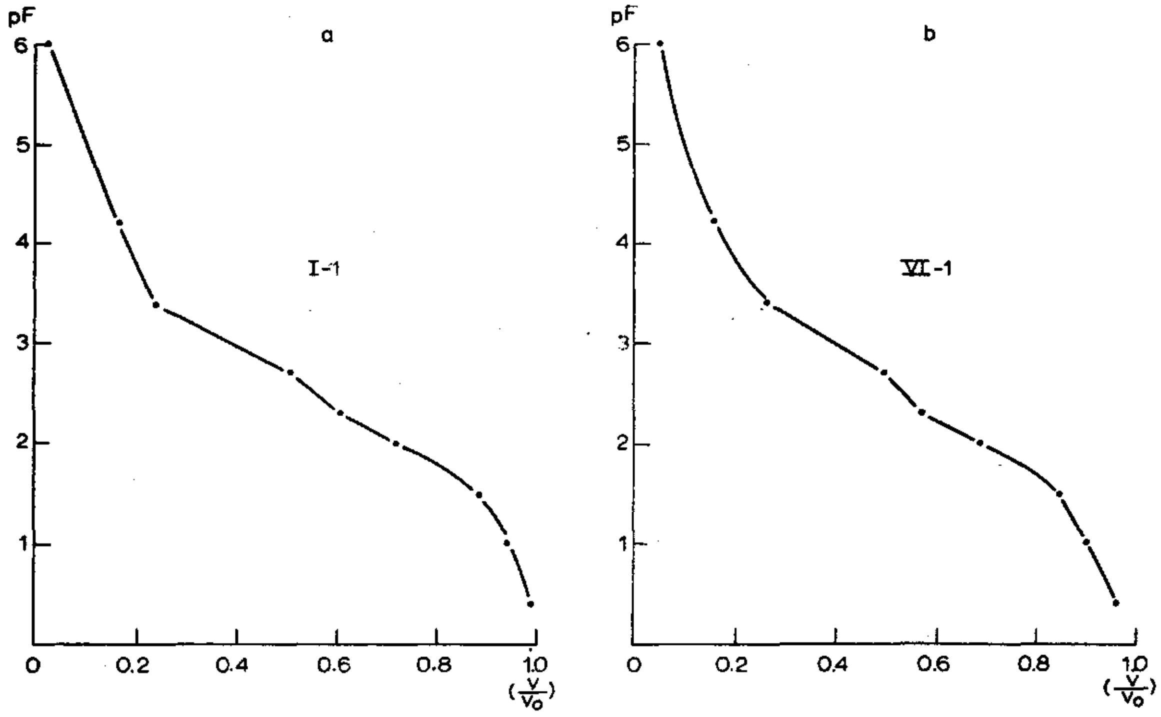

Fig. 2. Examples of desorption curves obtained by plotting the pF-value along the vertical axis and $\frac{v}{v_o}$ value along the horizontal axis (where v_o represents the total pore space). The data are the samples I-1 and VI-1 of STIBOKA in its communication nr. 8

(VI - 1)

pF	6.0	4.2	3.4	2.7	2.3	2.0	1.5	1.0	0.4	0
v	2.5	8.0	13.2	25.2	28.5	34.3	42.7	45.2	48.5	50.0
v/v_o	0.05	0.16	0.26	0.50	0.57	0.69	0.85	0.90	0.97	

(I - 1)

pF	6.0	4.2	3.4	2.7	2.3	2.0	1.5	1.0	0.4	0
v	1.6	8.2	11.8	24.4	2.93	34.6	42.8	45.5	47.8	48.3
v/v_o	0.03	0.17	0.24	0.51	0.61	0.72	0.89	0.94	0.99	

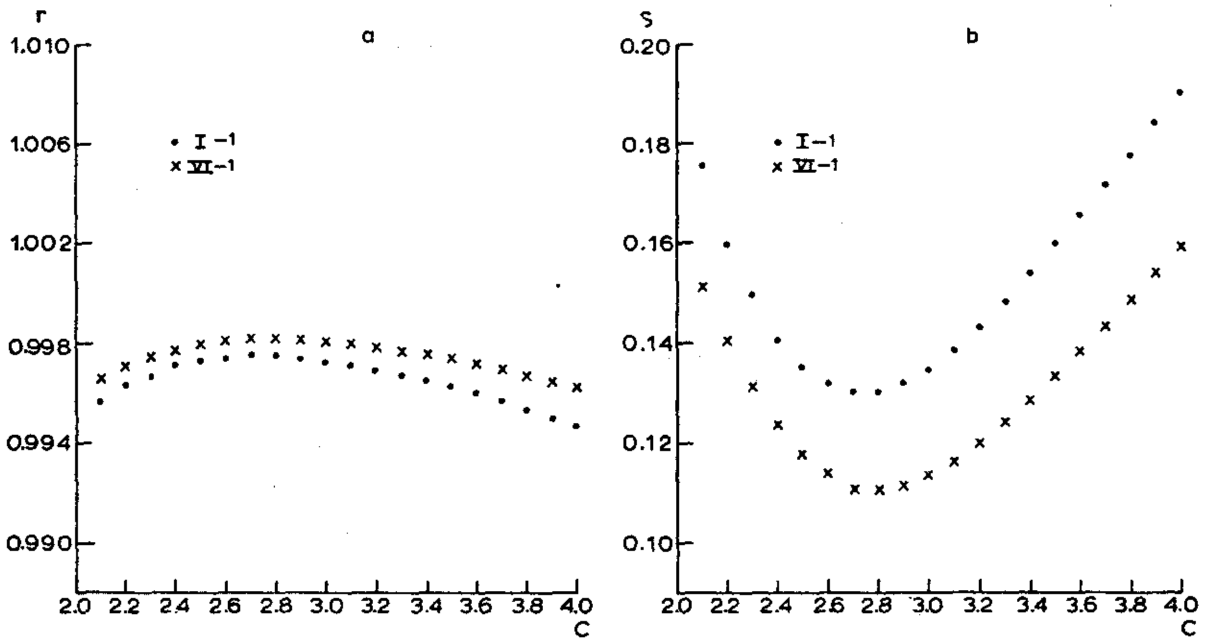

Fig. 3. (a) The correlation coefficient (r) between the experimental pF-values is calculated by linear regression for different values of constant c in equation (4) (in the range of $c = 2.1 \sim 4.0$)

(b) The standard deviation (S) between the experimental pF-values and the calculated pF-values is calculated for different values of constant c in equation (4) (in the range of $c = 2.1 \sim 4.0$). • symbols represent the case of sample (I-1) and x symbols represent the case of sample (VI-1)

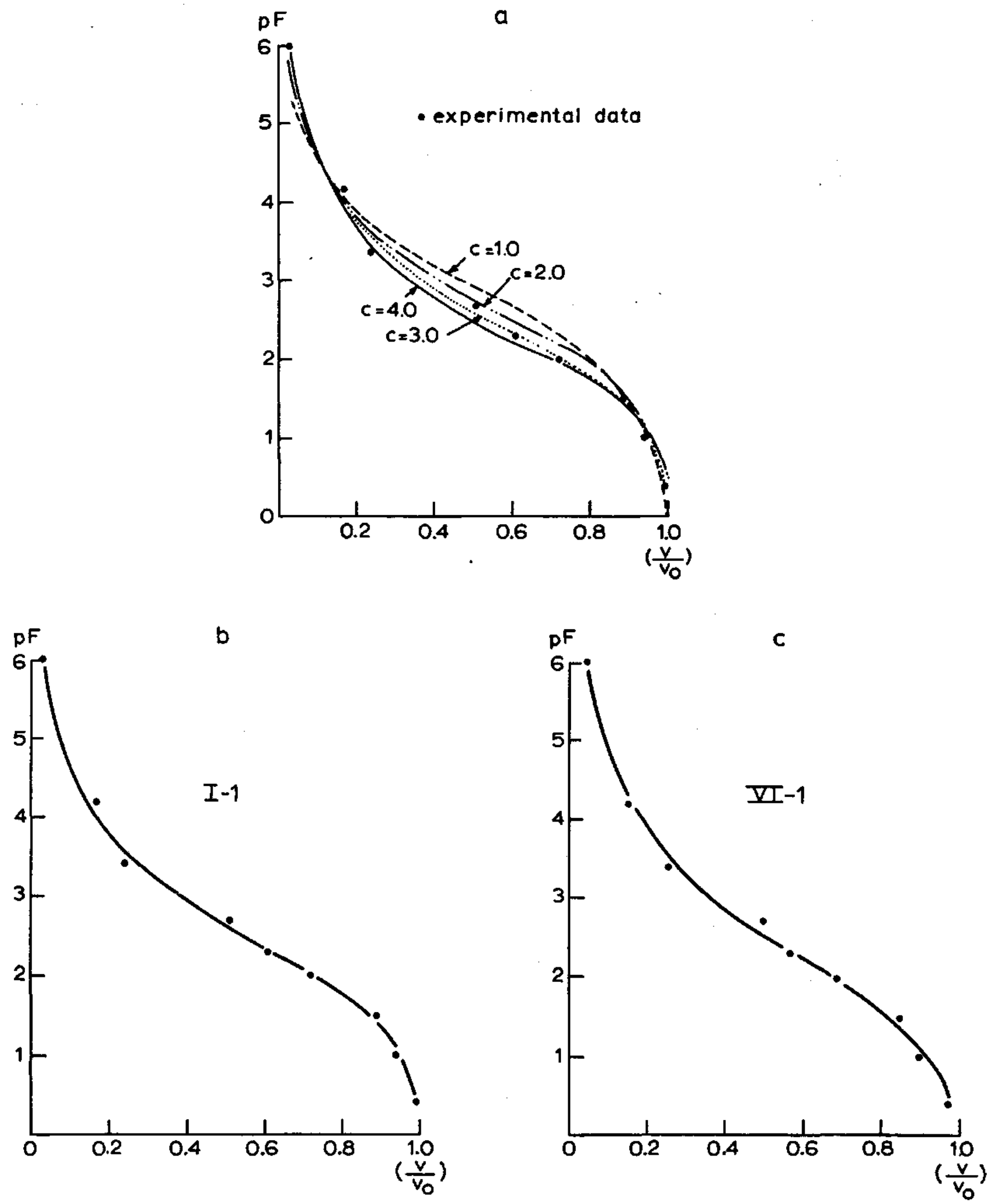

Fig. 4. (a) Desorption curves calculated by equation (4) using various values of c (c = 1.0, 2.0, 3.0, 4.0) for the sample I-1

(b) Desorption curve calculated by equation (4) when the c-value is equal to 2.8. $pF = 1.860 + 0.4276 \ln \left[\left(\frac{v}{v_o} \right)^{-2.8} - 1 \right]$. Sample I-1

(c) Desorption curve calculated by equation (4) when the c-value is equal to 2.8. $pF = 1.651 + 0.5097 \ln \left[\left(\frac{v}{v_o} \right)^{-2.8} - 1 \right]$. Sample VI-1

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2. CARY, J.W., R.A. KOHL and S.A. TAYLOR. 1964. Water adsorption by dry soil and its thermodynamic functions. Soil Sci. Soc. Am. Proc. 28: 309-314.
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