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Prediction of void ratio-osmotic pressure relationship of clays

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Abstract

The osmotic pressure or the repulsive pressure due to difference in concentration of ions between clay platelets and the bulk solution is popularly predicted by the use of Gouy-Chapman theory. The existing procedures are time consuming, difficult and laborious. In this paper a simple, quick and yet an accurate procedure has been presented to obtain the repulsive pressure at any value of d (half distance between clay platelets) or the void ratio or the *vice versa*. The results are obtained directly by using the figures and tables presented.

Key words : Clays, consolidation, osmotic pressure, electrolytes, void ratio.

1. Introduction

The relationship between the osmotic pressure and the distance between clay platelets is of importance in the field of soil science and soil engineering. Several research workers have shown that the Gouy-Chapman theory predicts reasonably well the relation between the repulsive pressure induced by the interaction of electric double layers and the distance between parallel clay platelets (or the equivalent void ratio)[1-6].

At present, the methods used to predict the relationship is essentially either the one suggested by Bolt[2] or the one by van Olphen[5]. These methods cannot be used directly and are difficult and time consuming. In this paper, an easier, quicker and yet accurate procedure is detailed to find the relation between the two variables, *viz.*, repulsive pressure (hereafter termed as simply pressure) and distance between the clay platelets (or the equivalent void ratio).

2. Bolt's procedure

(*a*) The distance between the clay platelets and the concentration of cations at the central plane between the platelets is related by

$$v\sqrt{\beta C_0}\,(x_0 + d) = 2\sqrt{C_0/C_c}\int_{\psi=0}^{\psi=\pi/2} \frac{d\psi}{\sqrt{1 - \left(\frac{C_0}{C_c}\right)^2 \sin^2\psi}} \qquad (1)$$

where

v = Valence of the cation

$\beta = \frac{8\pi F^2}{1000\epsilon RT} \simeq 1 \times 10^{15}$ cm/m mole at 20° C

F = Faraday's constant

ϵ = Dielectric constant of the pore fluid

d = Half distance between parallel clay platelets

R = Gas constant

T = Temperature

C_0 = Concentration of cations in the bulk liquid

C_c = Concentration of cations in the central plane

$x_0 \simeq 4/v\beta\Gamma$ [$= 1/v$ Å for illite, $2/v$ Å for kaolinite and $4/v$ Å for montmorillonite, 1 Å = 0·1 nm]

Γ = Surface density of charge in meq/cm^2

ψ = Variable related to the central concentration, the actual value of which is immaterial for the evaluation of this elliptic integral.

(*b*) The repulsive pressure is found as the difference between the osmotic pressure in the central plane and the osmotic pressure in the bulk solution. The osmotic pressure is found from vant Hoff's equation (equation 2)

$$p = RTC_0 (C_c/C_0 + C_0/C_c - 2). \tag{2}$$

(*c*) For saturated pure clays, the distance between the clay platelets can be expressed in terms of void ratio of the system as

$$e = G\gamma_w Sd \tag{3}$$

where

e = Void ratio

G = Specific gravity of soil particles

γ_w = Unit weight of water

S = Specific surface of soil.

Hence to find the void ratio of the system corresponding to the repulsive pressure of p, first equation (2) is used to find C_0/C_c then d is evaluated from equation (1) and finally e is found from equation (3). It is very difficult to find p for a given value of e and the procedure is time consuming. Further, the estimation of x_0 (equation 1) involves approximation.

3. van Olphen's procedure

van Olphen[5] has given tables, based on the Gouy-Chapman theory, for particular cases to find the relation between e and p. In summary, the procedure is as follows: The two important equations used are

$$\text{(i)} \quad \int_z^u (2\cosh y - 2\cosh u)^{-\frac{1}{2}} dy = -\int_0^d d\xi = -Kd$$

$$\text{(ii)} \quad -(dy/d\xi)_{x=0} = (2\cosh z - 2\cosh u)^{1/2} = \sigma\sqrt{2\pi/\epsilon nkT} \ (\text{at } x = 0,\ y = z) \tag{4}$$

where

$y = ve\phi/kT$; $u = ve\phi_m/kT$

$\xi = Kx$

ϕ = Electric potential at a distance x from clay surface

ϕ_m = Electric potential at midplane

$e = 4{\cdot}8 \times 10^{-10}$ esu

k = Boltzmann constant

$$K = \sqrt{8\pi ne^2v^2/\epsilon kT} \tag{5}$$

n = Concentration of ions in the pore fluid in molar

x = Distance measured from clay platelet.

van Olphen has given for particular values of $(dy/d\xi)_{x=0}$, a list of values for u, z and Kd. When void ratio e is given, d is found from equation (3) and K from equation 5; hence u can be estimated from corresponding values of $(dy/d\xi)_{x=0}$. Knowing the value of u, p can be determined by Langmuir's equation, *viz.*

$$p = 2nkT(\cosh u - 1) \tag{6}$$

It can be shown that equations 2 and 6 are one and the same.

The main difficulty in this method is that tables are not given for all values of $dy/d\xi$ and u. Hence interpolations are difficult and inaccurate.

4. Simplified procedure

(i) Known data are:

Table I (*a*)

Values of Kd or C_1e or C_2m for various values of u and $P/\sqrt{n\epsilon T}$

u	$P/\sqrt{n\epsilon T}$ (meq/100m² $\sqrt{°K}$ molar)								
	0·001	0·002	0·003	0·004	0·005	0·006	0·007	0·008	0·009
0·1	3·649	3·989	4·115	4·179	4·218	4·245	4·263	4·277	4·288
0·5	2·013	2·347	2·472	2·536	2·576	2·602	2·620	2·635	2·645
1·0	1·277	1·592	1·714	1·778	1·817	1·843	1·861	1·875	1·886
1·5	0·844	1·127	1·244	1·307	1·345	1·371	1·389	1·403	1·414
2·0	0·555	0·797	0·906	0·967	1·004	1·029	1·048	1·062	1·073
2·5	0·359	0·554	0·653	0·710	0·746	0·771	0·789	0·803	0·814
3·0	0·229	0·377	0·462	0·514	0·548	0·572	0·590	0·603	0·614
3·5	0·143	0·249	0·319	0·365	0·397	0·419	0·436	0·449	0·459
4·0	0·089	0·162	0·215	0·254	0·281	0·302	0·318	0·330	0·340
4·5	0·055	0·103	0·142	0·172	0·195	0·213	0·227	0·238	0·247
5·0	0·033	0·064	0·091	0·133	0·132	0·146	0·158	0·168	0·177
5·5	0·020	0·040	0·057	0·073	0·087	0·098	0·108	0·116	0·124
6·0	0·012	0·024	0·036	0·046	0·056	0·064	0·072	0·078	0·084
6·2	0·010	0·020	0·030	0·038	0·046	0·054	0·060	0·066	0·072
6·4	0·008	0·017	0·024	0·032	0·039	0·045	0·051	0·056	0·061
6·6	0·007	0·014	0·020	0·026	0·032	0·037	0·043	0·047	0·051
6·8	0·006	0·011	0·017	0·022	0·027	0·031	0·035	0·039	0·043
7·0	0·005	0·009	0·014	0·018	0·022	0·026	0·030	0·033	0·036
7·2	0·004	0·008	0·011	0·015	0·018	0·021	0·025	0·027	0·030
7·4	0·003	0·006	0·009	0·012	0·015	0·018	0·020	0·023	0·025
7·6	0·003	0·005	0·008	0·010	0·012	0·015	0·017	0·019	0·021
7·8	0·002	0·004	0·006	0·008	0·010	0·012	0·014	0·016	0·017
8·0	0·002	0·003	0·005	0·007	0·008	0·010	0·011	0·013	0·014
8·5	0·001	0·002	0·003	0·004	0·005	0·006	0·007	0·008	0·009
9·0	0·001	0·001	0·002	0·003	0·003	0·004	0·004	0·005	0·006
9·5			0·001	0·002	0·002	0·002	0·003	0·003	0·003
10·0			0·001	0·001	0·001	0·001	0·002	0·002	0·002
10·5				0·001	0·001	0·001	0·001	0·001	0·001
11·0							0·001	0·001	0·001
11·5									0·001

The soil properties are: the base exchange capacity, BEC in meq/100 gm and the surface area, S in m²/gm and γ, the density of soil particles.

Let $P = \text{BEC}/S$ in meq/100 m².

In other words, this is expressed as charge density, σ in esu/cm².

Table I (*b*)

Values of Kd or C_1e or C_2m for various values of u and $P/\sqrt{n\epsilon T}$

u	$P/\sqrt{n\epsilon T}$ (meq/100m² $\sqrt{°K}$ molar)								
	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
0·1	4·297	4·336	4·350	4·356	4·360	4·363	4·364	4·366	4·367
0·5	2·654	2·694	2·707	2·714	2·718	2·720	2·722	2·723	2·724
1·0	1·895	1·935	1·948	1·955	1·958	1·961	1·963	1·964	1·965
1·5	1·423	1·463	1·476	1·482	1·486	1·489	1·491	1·492	1·493
2·0	1·081	1·121	1·134	1·141	1·145	1·147	1·149	1·151	1·152
2·5	0·822	0·862	0·875	0·881	0·885	0·888	0·890	0·891	0·892
3·0	0·623	0·662	0·675	0·681	0·685	0·688	0·690	0·691	0·692
3·5	0·468	0·506	0·519	0·526	0·530	0·533	0·534	0·536	0·537
4·0	0·348	0·386	0·399	0·405	0·409	0·412	0·414	0·415	0·416
4·5	0·255	0·292	0·305	0·311	0·315	0·318	0·320	0·321	0·322
5·0	0·184	0·219	0·232	0·238	0·242	0·245	0·246	0·248	0·249
5·5	0·130	0·162	0·175	0·181	0·185	0·188	0·189	0·191	0·192
6·0	0·089	0·119	0·130	0·137	0·141	0·143	0·145	0·146	0·148
6·2	0·076	0·104	0·116	0·122	0·126	0·128	0·130	0·132	0·133
6·4	0·065	0·091	0·102	0·109	0·112	0·115	0·117	0·118	0·119
6·6	0·055	0·079	0·090	0·096	0·100	0·103	0·105	0·106	0·107
6·8	0·047	0·069	0·080	0·086	0·089	0·092	0·094	0·095	0·096
7·0	0·039	0·060	0·070	0·076	0·079	0·082	0·084	0·085	0·086
7·2	0·033	0·051	0·061	0·067	0·070	0·073	0·075	0·076	0·077
7·4	0·028	0·044	0·053	0·059	0·062	0·065	0·067	0·068	0·069
7·6	0·023	0·038	0·046	0·052	0·055	0·057	0·059	0·061	0·062
7·8	0·019	0·032	0·040	0·045	0·048	0·051	0·053	0·054	0·055
8·0	0·016	0·027	0·035	0·039	0·043	0·045	0·047	0·048	0·049
8·5	0·010	0·018	0·023	0·027	0·030	0·032	0·034	0·035	0·036
9·0	0·006	0·011	0·016	0·019	0·021	0·023	0·024	0·026	0·027
9·5	0·004	0·007	0·010	0·012	0·014	0·016	0·017	0·018	0·019
10·0	0·002	0·004	0·006	0·008	0·010	0·011	0·012	0·013	0·013
10·5	0·001	0·003	0·004	0·005	0·006	0·007	0·008	0·009	0·009
11·0	0·001	0·002	0·002	0·003	0·004	0·005	0·005	0·006	0·006
11·5		0·001	0·002	0·002	0·002	0·003	0·003	0·004	0·004

Since

$$1 \ \frac{\text{meq}}{100 \ \text{m}^2} = 289104 \ \text{esu/cm}^2$$

$$\sigma = 289104\text{P} \quad (\text{esu/cm}^2) \tag{4}$$

(ii) Since

$$-(dy/d\xi)_{\xi=0} = \sigma \sqrt{2\pi/\epsilon nkT}.$$

Table I (c)

Values of Kd or C_1e or C_2m for various values of u and $P/\sqrt{n\epsilon T}$

u	$P/\sqrt{n\epsilon T}$ (meq/100 m^2 $\sqrt{^{\circ}K}$ molar)								
	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0·1	4·368	4·371	4·373	4·373	4·374	4·374	4·374	4·374	4·374
0·5	2·725	2·729	2·730	2·731	2·731	2·732	2·732	2·732	2·732
1·0	1·966	1·970	1·972	1·972	1·973	1·973	1·973	1·973	1·973
1·5	1·494	1·498	1·500	1·500	1·501	1·501	1·501	1·501	1·501
2·0	1·152	1·157	1·158	1·158	1·159	1·159	1·159	1·159	1·160
2·5	0·893	0·897	0·898	0·899	0·900	0·900	0·900	0·900	0·900
3·0	0·693	0·697	0·698	0·699	0·699	0·700	0·700	0·700	0·700
3·5	0·538	0·542	0·543	0·544	0·544	0·544	0·545	0·545	0·545
4·0	0·417	0·421	0·422	0·423	0·423	0·424	0·424	0·424	0·424
4·5	0·323	0·327	0·328	0·329	0·329	0·330	0·330	0·330	0·330
5·0	0·250	0·254	0·255	0·256	0·256	0·256	0·257	0·257	0·257
5·5	0·193	0·197	0·198	0·199	0·199	0·199	0·200	0·200	0·200
6·0	0·148	0·152	0·154	0·154	0·155	0·155	0·155	0·155	0·155
6·2	0·134	0·138	0·139	0·140	0·140	0·140	0·140	0·141	0·141
6·4	0·120	0·124	0·125	0·126	0·126	0·127	0·127	0·127	0·127
6·6	0·108	0·112	0·113	0·114	0·114	0·115	0·115	0·115	0·115
6·8	0·097	0·101	0·102	0·103	0·103	0·104	0·104	0·104	0·104
7·0	0·087	0·091	0·092	0·093	0·093	0·094	0·094	0·094	0·094
7·2	0·078	0·082	0·083	0·084	0·084	0·085	0·085	0·085	0·085
7·4	0·070	0·074	0·075	0·076	0·076	0·076	0·077	0·077	0·077
7·6	0·062	0·066	0·068	0·068	0·069	0·069	0·069	0·069	0·069
7·8	0·056	0·060	0·061	0·062	0·062	0·062	0·062	0·063	0·063
8·0	0·050	0·054	0·055	0·056	0·056	0·056	0·056	0·057	0·057
8·5	0·037	0·041	0·042	0·043	0·043	0·044	0·044	0·044	0·044
9·0	0·027	0·031	0·032	0·033	0·033	0·034	0·034	0·034	0·034
9·5	0·020	0·023	0·025	0·025	0·026	0·026	0·026	0·026	0·026
10·0	0·014	0·017	0·019	0·019	0·020	0·020	0·020	0·020	0·020
10·5	0·010	0·013	0·014	0·015	0·015	0·015	0·015	0·016	0·016
11·0	0·007	0·009	0·010	0·011	0·011	0·012	0·012	0·012	0·012
11·5	0·004	0·006	0·008	0·008	0·008	0·009	0·009	0·009	0·009

From equations 4 and 7 it can be written

$$-(dy/d\xi)_{\xi=0} = (2\cosh z - 2\cosh u)^{1/2}$$

$$= 2513 \cdot 61 \; P/\sqrt{\epsilon n T} \qquad (8)$$

where

$P = BEC/S$ in meq/100m^2

ϵ = The dielectric constant of the medium

n = Concentration of ion in molar

T = Temperature in degree Kel in.

(iii) The pore fluid property K is given by equation (5) and can be written as[7].

$K = 50 \cdot 272\, v \sqrt{n/\epsilon T}$ in $1/\text{Å}$

or $502 \cdot 72\, v \sqrt{n/\epsilon T}$ in $1/nm$. (9)

(iv) Equation 3 can be written as

$d = e/\gamma S$

where

γ = Density of soil solids and the non-dimensional parameter

Kd = becomes $Ke/\gamma S$ or $C_1 e$

where

$C_1 = K\gamma S$, a dimensionless quantity.

Since

$e = mG$, (where m = moisture content)

$Ke/\gamma S$ can also be written as $C_2 m$

where

$C_2 = K/\gamma_w S$ and γ_w = density of water

(v) Since $p = 2nkT (\cosh u - 1)$

$p/nT = 0 \cdot 1694544 (\cosh u - 1)$

where

p is in kg/cm^2

n is in molar

and T is in degree Kelvin.

Figure 1 (*a-c*) and table 1 (*a-c*) present relationship between Kd or $C_1 e$ or $C_2 m$ and $P/\sqrt{n\epsilon T}$ for various values of u. These tables and figures have been prepared by numerical integration using DEC system 1090 computer. Knowing the soil and fluid properties, *viz.*, $P/\sqrt{n\, \epsilon\, T}$ and K and the half distance between the platelets d, the non-dimensional parameter $u (= ve\ \varphi_m/kT)$ representing the midplane potential could be determined. Knowing u values, p/nT could be determined either from table II or fig. 2. For lower values of u, curve 1 and for higher values of u curve 2 could be used. In table II the values of p/nT could be taken as linearly varying in between two successive values of u. This does not lead to any error of practical significance. It should be mentioned here that the surface area determined either by nitrogen absorption method (BET) or water vapour absorption method or ethylene glycol absorption method[8] varies and does not result in an unique value. Further, the surface area does depend on the nature

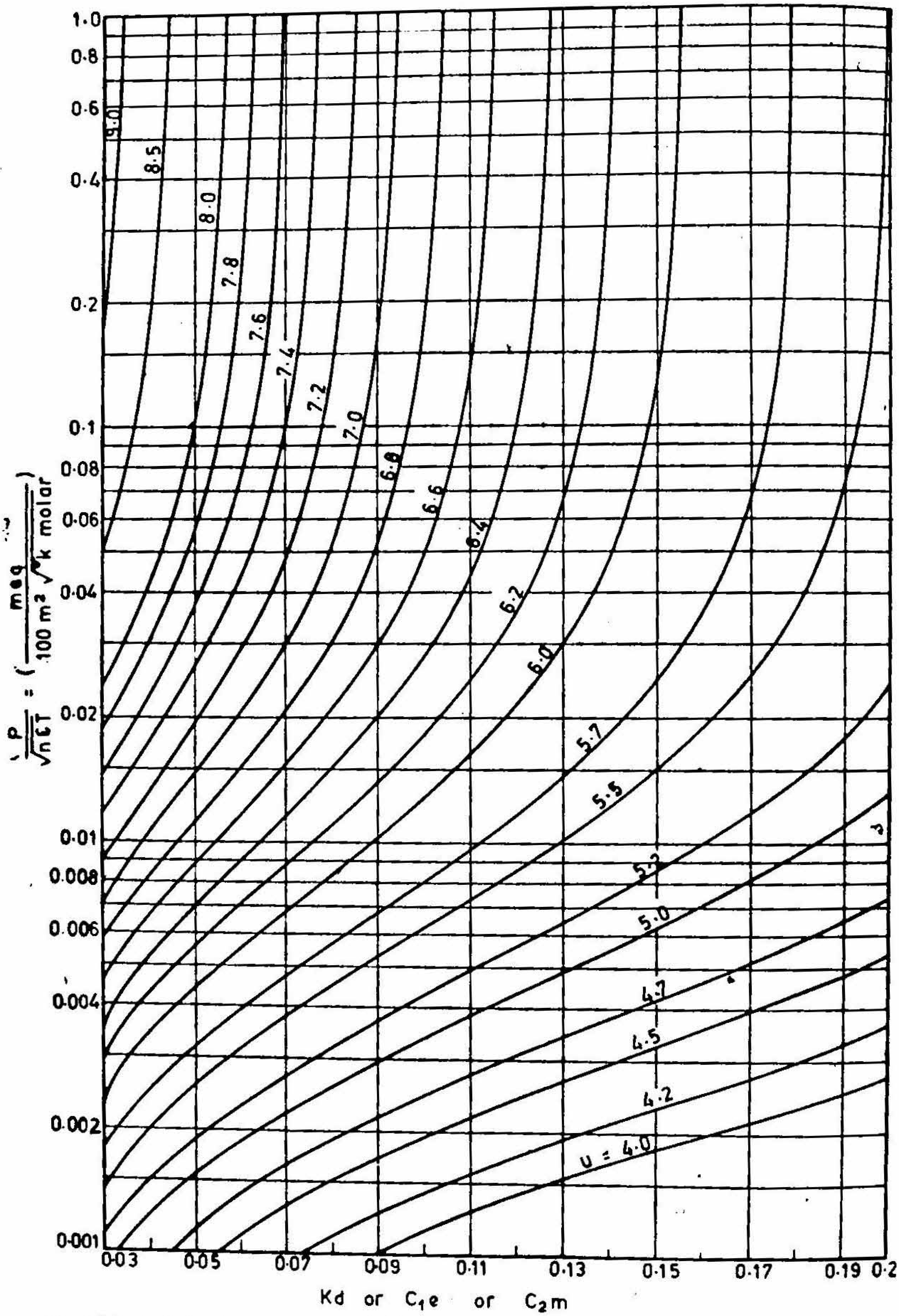

FIG. 1 (*a*). Relationship between $P/\sqrt{n\epsilon T}$ and Kd or C_1e or C_2m for various values of u.

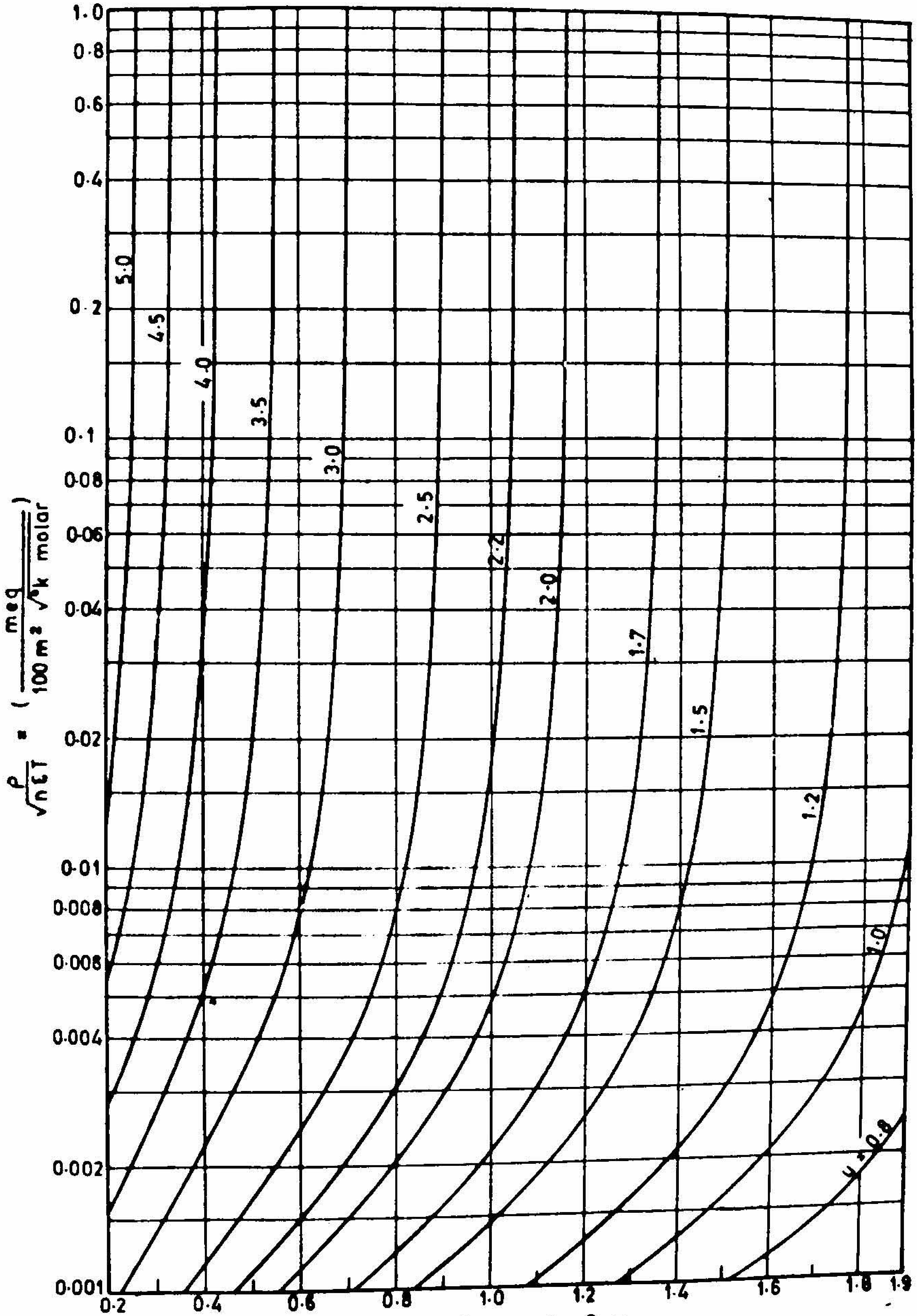

FIG. 1 (*b*). Relationship between $P/\sqrt{n\epsilon T}$ and Kd or C_1e or C_2m for various values of u.

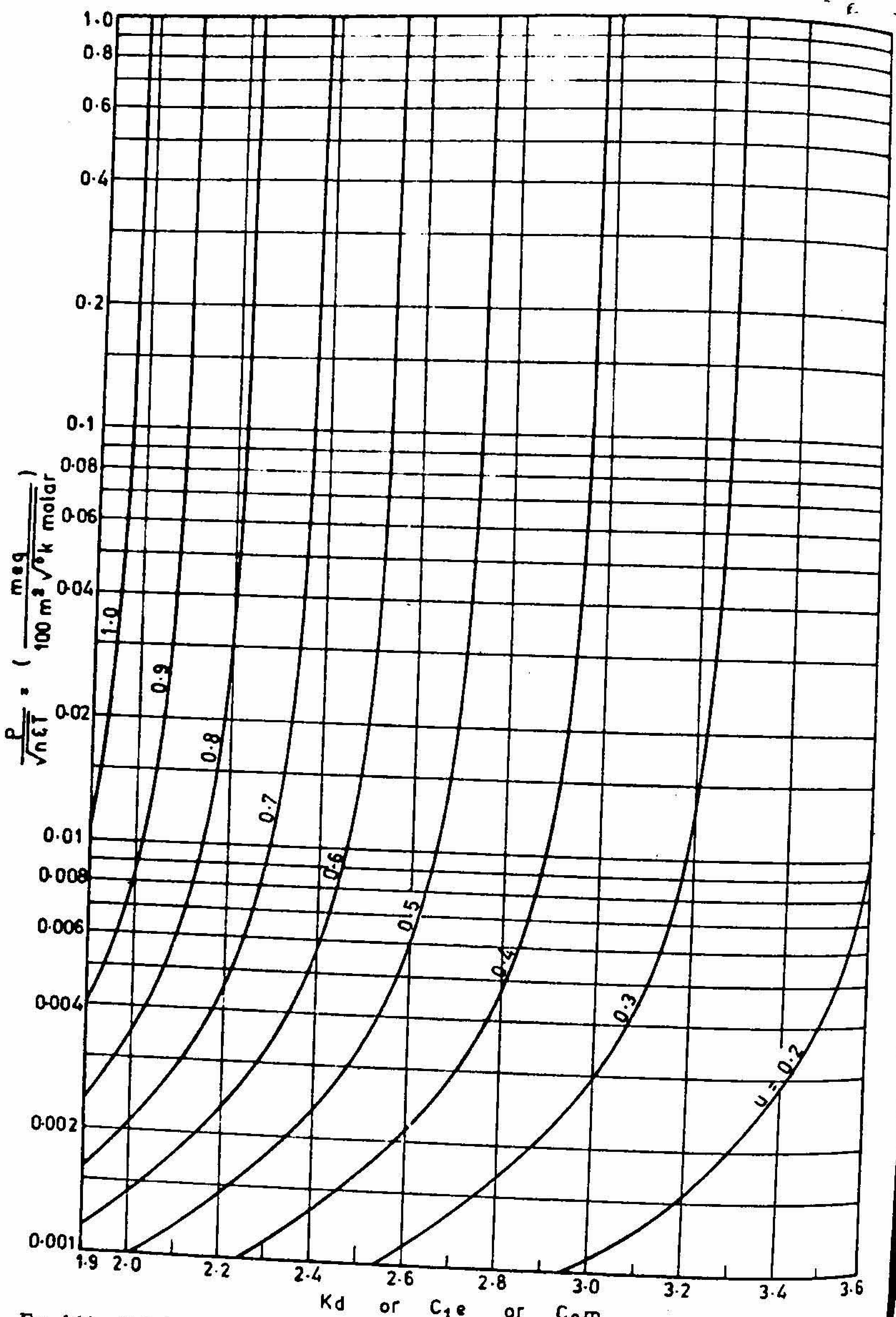

FIG. 1 (c). Relationship between $P/\sqrt{n\epsilon T}$ and Kd or C_1e or C_2m for various values of u.

Table II

Values of P/nT (kg/cm^2/°K molar) for various values of u

u†	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0·0	0	0·0008	0·0034	0·0077	0·0137	0·0216	0·0314	0·0432	0·0572	0·0734
1·0	0·0920	0·1133	0·1374	0·1645	0·1950	0·2292	0·2673	0·3098	0·3571	0·4097
2·0	0·4681	0·5328	0·6046	0·6841	0·7722	0·8697	0·9776	1·0970	1·2290	1·3751
3·0	1·5366	1·7151	1·9126	2·1308	2·3721	2·6389	2·9337	3·2596	3·6198	4·0180
4·0	4·4580	4·9444	5·4820	6·0761	6·7327	7·4584	8·2604	9·1468	10·127	11·209
5·0	12·406	13·728	15·190	16·805	18·590	20·563	22·743	25·153	27·816	30·759
6·0	34·012	37·607	41·580	45·971	50·823	56·186	62·113	68·664	75·903	83·903
7·0	92·745	102·52	113·32	125·25	138·44	153·02	169·13	186·94	206·62	228·36
8·0	252·40	278·96	308·32	340·76	376·62	416·25	460·04	508·44	561·93	621·05
9·0	686·38	758·59	838·39	926·58	1024·0	1131·8	1250·8	1382·4	1527·8	1688·5
10·0	1866·1	2062·3	2279·3	2519·0	2783·9	3076·7	3400·3	3758·0	4153·2	4590·0
11·0	5072·8	5606·3	6196·0	6847·6	7567·8	8363·8	9243·4	10216·0	11290·0	12477·0

† Read u values first vertically down and then horizontally towards right, *e.g.*, u = 6·2, value of p/nT = 41·58 ; for u = 8·4, p/nT = 376·62. For in between values of u, linear interpolation is valid.

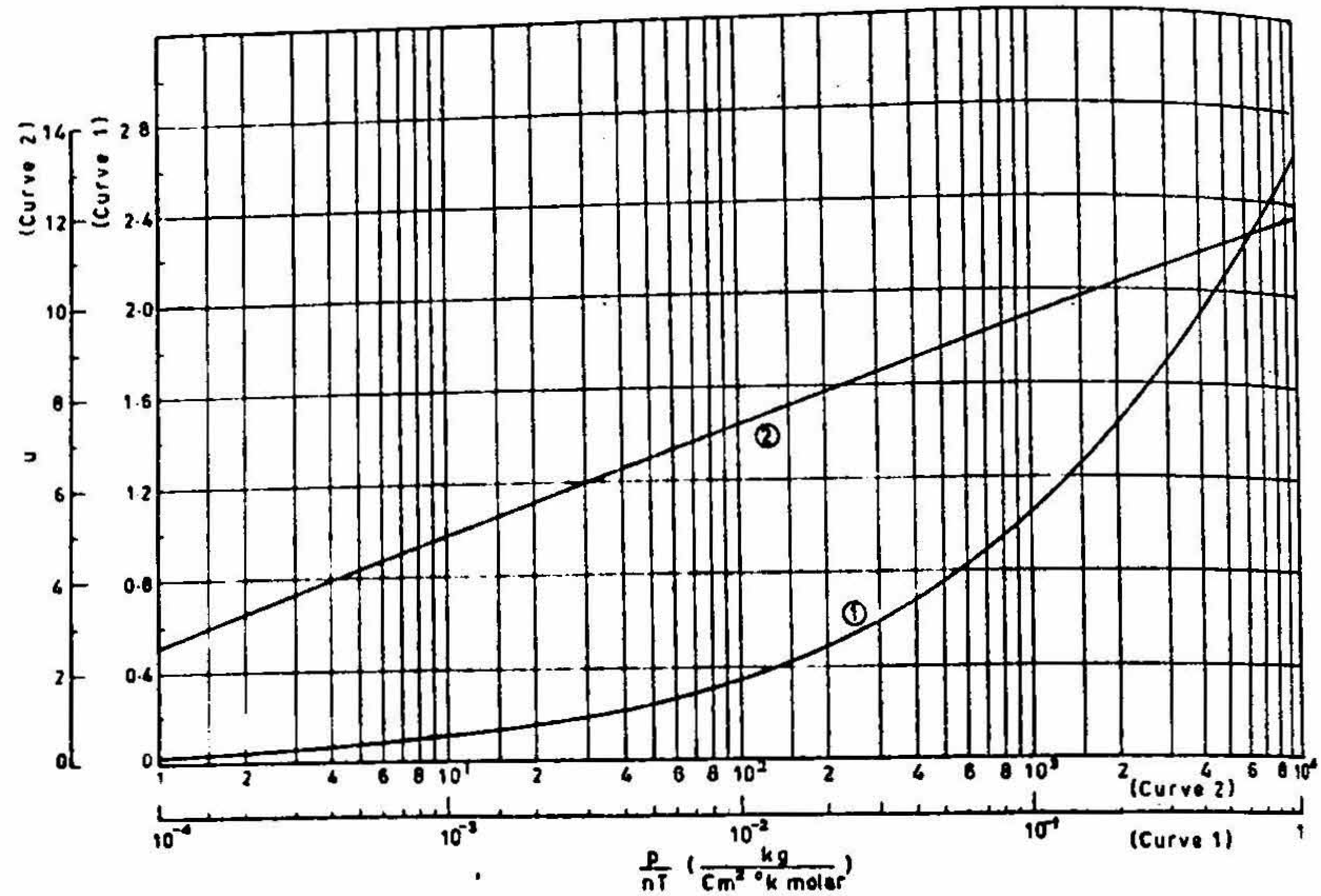

FIG. 2. Relationship between P/nT and u.

of exchangeable cations. Thus, variations are possible in determining the values of P for natural soils.

Two worked out examples are given in Appendix I.

5. Conclusion

A simple, quick and yet an accurate procedure has been presented to obtain the repulsive pressure at any value of d (half distance between clay platelets) or the void ratio e or the *vice versa* using the Gouy-Chapman theory. The procedure directly yields the result either by referring to two tables or two figures prepared in this study.

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Appendix I

Example 1

To determine the repulsive pressure exhibited by a montmorillonite clay at a void ratio of 5·0 given the following data. Base exchange capacity (BEC) = 100 meq/100 gm, Surface area (S) = 800 m²/gm, density of soil solids (γ) = 2·7 gm/cc (2·7 × 10⁶ gm/m³), concentration of ions in the pore fluid (n) = 0·0001 molar, valence of cation (V) = 1, dielectric constant of pore medium (ϵ) = 78·54 (at a temperature of 25° C), Temperature (T) = 25° C = 298° K.

Solution

Step 1 Determine $P/\sqrt{\epsilon n T}$

$$P/\sqrt{\epsilon nT} = \mathrm{BEC}/S\sqrt{\epsilon nT} = 100/800\sqrt{78\cdot 54 \times \cdot 0001 \times 298}$$

$$= 0\cdot 0817 \ \mathrm{meq}/100\ \mathrm{m}^2\ \sqrt{K^\circ\ \mathrm{molar}}$$

Step 2 Determine Kd or C_1e

From equation 10,

$$K = 50\cdot 272\ v\sqrt{n/\epsilon T}$$

$$= 50\cdot 272 \times 1\sqrt{0\cdot 0001/78\cdot 54 \times 298}$$

$$= 0\cdot 003286\ 1/\text{Å}$$

$$= 3\cdot 286 \times 10^7\ 1/\mathrm{m}$$

$$C_1e = (K/\gamma S)\,e \text{ or } \frac{3\cdot 286 \times 10^7}{2\cdot 7 \times 10^6 \times 800} \times 5\cdot 0$$

$$= 0\cdot 07605$$

Step 3 From fig. 1(*a*) or table I (*b*) for $P/\sqrt{\epsilon nT} = 0 \cdot 0817$ and $C_1 e = 0 \cdot 07605$, the value of $u = 7 \cdot 2$.

Step 4 From table II for $u = 7 \cdot 2$, $p/nT = 113 \cdot 32$ and hence $p = 3 \cdot 38$ kg/cm². Figure 2 could also be used to get the values of p/nt.

Example 2

To determine the void ratio and half space distance d, exhibited by an illite clay at a repulsive pressure of 1 kg/cm² given the following data. Base exchange capacity (BEC) = 40 meq/100 gm, Surface area (S) = 100 m²/gm, density of soil solids (γ) = 2·7 gm/cc, concentration of ions in the pore fluid (n) = 0·0001 molar. Valency of cation (ν) = 1. Dielectric constant of pore fluid (ϵ) = 78·54, temperature (T) = 25° C or 298° K.

Solution

Step 1 $p/nT = 1/\cdot 0001 \times 298 = 33 \cdot 557$.

From Table 2, for $p/nT = 33 \cdot 557$ the interpreted value of $u = 5 \cdot 986$ or $6 \cdot 0$. From fig. 2 the same value is obtained.

Step 2 $P/\sqrt{\epsilon nT} = \text{BEC}/S\sqrt{\epsilon nT} = 40/100 \sqrt{78 \cdot 54 \times \cdot 0001 \times 298}$

$$= 0 \cdot 2615$$

Step 3 From fig. 1 (*a*) or table I (*c*) for $u = 6 \cdot 0$ and $P/\sqrt{\epsilon nT} = 0 \cdot 2615$, Kd or $C_1 e$ = 0·1532.

Step 4 $K = 50 \cdot 272 \, \nu \sqrt{n/\epsilon T} \ldots 1/\text{Å}$

$$= 50 \cdot 272 \times 1 \times \sqrt{0 \cdot 0001/78 \cdot 54 \times 298}$$

$$= 0 \cdot 003286$$

Hence

$$d = 0 \cdot 1532/0 \cdot 003286 = 46 \cdot 62 \text{ Å} = 4 \cdot 662 \text{ nm}$$

$$C_1 = K/\gamma S = 0 \cdot 003286 \times 10^{10}/2 \cdot 7 \times 10^6 \times 100$$

$$= 0 \cdot 1217.$$

Hence

$$e = 0 \cdot 1532/0 \cdot 1217 = 1 \cdot 259$$

or $m = e/G = 1 \cdot 259/2 \cdot 7 = 0 \cdot 4663$

or 46·63%.