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A. S. Said[a]
[a] CHEMICAL ENGINEERING DEPARTMENT, UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN, SAUDI ARABIA

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Contribution to the Theory of Nonlinear Chromatography

A. S. SAID

CHEMICAL ENGINEERING DEPARTMENT
UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN, SAUDI ARABIA

Abstract

A new approach to the theory of nonlinear chromatography is presented. It applies to isotherms which are not too nonlinear, in which case it is shown that the center of gravity of the peak moves at a relative velocity equal to $1/\sqrt{2}$ of the velocity of peak maximum. Equations relating peak retention time, asymmetry, and peak shape in terms of the nonlinearity constant β, plate number N, and base capacity ratio k_0 are derived. The derived equations are checked by comparing them with the exact answers obtained from the numerical solution of the differential equations of the plate model applied to the nonlinear isotherm. The deviations are found to be small. It is also demonstrated that for slightly nonlinear isotherms, the resulting peak shapes are asymmetric Poisson distributions with asymmetries which can be calculated from the above-mentioned parameters.

The theory of nonlinear chromatography is quite complex and the differential equations involved have no analytic solutions. In spite of simplifying assumptions, the derived equations are still difficult and not too accurate.

Different approaches need to be explored. It is felt that simplifying assumptions should be made from the start instead of starting with the exact differential equations after which a succession of approximations is made to get an equation of reasonable complexity. The validity of the simplifying assumptions made is tested by comparing the derived equations with the results obtained from the numerical solution of the exact differential equations. The plate theory applied to the nonlinear isotherm should be a good means for testing these assumptions because it lends itself to easy numerical solution, particularly when the plate model and not the stage model is used in the numerical analysis. In the plate model (*1*), equilibrium is assumed to occur only at the plates while the mobile phase moves continuously and without mixing between the plates.

The first application of the plate theory to the nonlinear isotherm was made by this author and co-worker (*2*, *3*). The numerical solution was described and the computer output data were plotted. Qualitative and semiempirical relations between the Langmuir constants and the asymmetry of the resulting peaks were given. The paper was published only as a company report.

Recently, a group of Russian scientists (*4*) published some papers on the same subject, namely on the application of the plate theory to the nonlinear isotherm. They also used a high-speed computer for the numerical calculations, but details of the numerical solution and program were not given. They presented curves which show the asymmetry of the peaks for different nonlinearity constants. No attempt was made to deduce quantitative relations between these constants and peak asymmetry.

In this paper the numerical solution is described and the FORTRAN program is given. Tables and plots of the output data are presented. The numerical solution is not given here as an alternative to analytic solutions but as a means of testing assumptions made in the course of deriving equations for the nonlinear isotherm.

DEVELOPMENT OF THE DIFFERENTIAL-DIFFERENCE EQUATION FOR THE NONLINEAR ISOTHERM ACCORDING TO THE PLATE MODEL

A differential material balance around plate n gives (*1*)

$$(C_{n-1} - C_n)\,dv = d\left(x_n \frac{S}{N}\right) \tag{1}$$

C_n is the concentration of solute in the mobile phase in equilibrium with the solute adsorbed on plate n. v is the volume of mobile phase that has crossed the plate from the start, x_n is the concentration of solute in the stationary phase on plate n, S is the total weight of the stationary phase, and N is the total plate number.

We will be concerned with adsorption isotherms which are not too nonlinear. In this case the Langmuir isotherm is sufficient so that

$$x_n = \frac{k_0 C_n}{1 + bC_n} \tag{2}$$

k_0 is the base capacity ratio (at zero concentration) and b is a constant.

Substituting from Eq. (2) into Eq. (1) and making the following substitutions

$$X_n = x_n/x_1{}^0$$
$$u = Nv/Sk_0$$
$$\beta = -bx_1{}^0/k_0$$

where $x_1{}^0$ is the initial concentration of solute on Plate 1, one finally gets

$$\frac{dX_n}{du} = \frac{X_{n-1}}{1 + \beta X_{n-1}} - \frac{X_n}{1 + \beta X_n} \tag{3}$$

or

$$\frac{dX_n}{du} = -\nabla_n \frac{X}{1 + \beta X} \tag{4}$$

∇_n is the first backward difference with respect to n.

NUMERICAL SOLUTION OF THE COMBINED DIFFERENCE-DIFFERENTIAL EQ. (4)

We shall confine ourselves to the simple case where Plate 1 only is loaded with solute at the start. In this case

$$x_1{}^0 \frac{S}{N} = \int_0^\infty C_n \, dv$$

If we define a relative effluent concentration by the formula

$$Y_n = C_n k_0/x_1{}^0 \tag{5}$$

then

$$Y_n = \frac{X_n}{1 + \beta X_n} \tag{6}$$

and

$$\int_0^\infty Y_n \, du = 1 \tag{7}$$

If the isotherm is linear $\beta = 0$ and $Y_n = X_n$, the solution is the Poisson distribution function, namely

$$Y_n = e^{-u} \frac{u^N}{N!} \tag{8}$$

For the general case where $\beta \neq 0$, there is no analytic solution but a numerical solution is obtained as follows.

The boundary conditions of the problem are

I $$X(n, 0) = \begin{cases} 1 & \text{for } n = 1 \\ 0 & \text{for } n > 1 \end{cases}$$

II $$X(0, u) = 0$$

Boundary Condition I states that the first plate only is loaded with solute at the start and Boundary Condition II states that the concentration of solute in the mobile phase entering the column is always equal to 0.

If $X(n, u)$ is known, it is possible to calculate $X(n, u + \Delta u)$ using Taylor series as follows:

$$X(n, u + \Delta u) = X(n, u) + \Delta u \dot{X}(n, u) + \frac{(\Delta u)^2}{2!} \ddot{X}(n, u) + \cdots \tag{9}$$

$\dot{X}$, $\ddot{X}$, ... are the first second, etc. derivatives of X with respect to u. For higher derivatives we use the symbol $X^{(r)}$ to denote the rth derivative.

Differentiating Eq. (4) leads to

$$\ddot{X}(n, u) = -\nabla_n \frac{\dot{X}}{(1 + \beta X)^2} \tag{10}$$

Differentiating again, one gets

$$\dddot{X}(n, u) = -\nabla_n \frac{\ddot{X}(1 + \beta X) - 2\beta \dot{X}^2}{(1 + \beta X)^3} \tag{11}$$

and so on.

It is evident that in order to calculate $X(n, u + \Delta u)$, one needs the values of $X(n, u)$, $X^{(r)}(n, u)$, $X(n - 1, u)$, and $X^{(r)}(n - 1, u)$, but the smaller the value of Δu, the less the number of terms in Eq. (9) needed for the same accuracy.

One deduces also that

III $$X^{(r)}(0, u) = 0, \qquad \text{for } r \geqslant 0$$

which is the third boundary condition. We have now all the data, formulas, and boundary conditions necessary for the numerical solution of Eq. (4). The FORTRAN program is given in Table 1. Values of X were calculated for u values up to 100 and for $\beta = -0.4, -0.2, 0, +0.5$. Table 2 gives a sample of the format, and Table 3 was prepared from the voluminous output data. Y values were deduced from the output X values using Eq. (6). The value of $\beta = 0$ was included intentionally, even though

TABLE 1

The FORTRAN Program for the Numerical Solution of Eq. (4)

```
      REAL*8  U, U1, Y, Y1, B1, B2, B3, B4, A1, A2, A3, X1, X2
      REAL*8  DLT
      DIMENSION  Y(2, 201), Y1(201), C(3), U(2)
      READ(1, 1)  (C(I), I = 1, 4), L
    1 FORMAT(4F4.1, I4)
      DO  100  M = 1, 4
      DLT = 0.01
      IX = 0
      U(1) = 0.0
      DO  2  J = 1, 201
    2 Y(1, J) = 0.0
      Y(1, 2) = 1.0
      WRITE(14)  U(1), (Y(1, J), J = 1, 25)
      WRITE(14)  (Y(1, J), J = 26, 51)
      WRITE(14)  (Y(1, J), J = 52, 77)
      WRITE(14)  (Y(1, J), J = 78, 101)
      WRITE(14)  (Y(1, J), J = 102, 126)
      WRITE(14)  (Y(1, J), J = 127, 152)
      WRITE(14)  (Y(1, J), J = 153, 178)
      WRITE(14)  (Y(1, J), J = 179, 201)
      DO  50  N = 1, L
      U(2) = U(1) + DLT
      Y(2, 1) = 0.0
      A1 = 0.0
      A2 = 0.0
      A3 = 0.0
      DO  60  J = 1, 200
      X1 = 1.0 + C(M)*Y(1, J)
      X2 = 1.0 + C(M)*Y(1, J + 1)
      B1 = ((Y(1, J)*1000.0)/X1) - ((Y(1, J + 1)*1000.0)/X2)
      B1 = B1/1000.0
      B2 = (((A1*1000.0)/X1)/X1) - (((B1*1000.0)/X2)/X2)
      B2 = B2/1000.0
      B3 = (A2*1000.0*X1 - 2000.0*A1*C(M)*A1)/(X1*X1*X1) -
      (B2*1000.0*X2 - 2000.0*B1*C(M)*B1)/(X2*X2*X2)
      B3 = B3/1000.0
      B4 = (((A3*1000.0*X1 - 6000.0*C(M)*A1*A2)*X1) + (6000.0*
      C(M)*A1*C(M)*A1*A1))/(X1*X1*X1) - (((B3*1000.0*X2 -
      6000.0*C(M)*B1*B2)*X2) + (6000.0*C(M)*B1*C(M)*B1*B1))/
      (X2*X2*X2)
      B4 = B4/1000.0
      Y(2, J + 1) = Y(1, J + 1)*1000.0 + DLT*1000.0*B1 + (((DLT*
      1000.0*B2)/2.0)*DLT) + (((DLT*1000.0*DLT*B3)/6.0)*DLT) +
      (((DLT*1000.0*B4*DLT)/6.0)*(DLT/4.0)*DLT)
      Y(2, J + 1) = Y(2, J + 1)/1000.0
      A1 = B1
      IF(Y(2, J + 1).LT.0.0)  Y(2, J + 1) = 0.0
      A2 = B2
```

(continued)

TABLE 1 (continued)

```
      A3 = B3
   60 CONTINUE
      WRITE(14)  U(2), (Y(2, J), J = 1, 25)
      WRITE(14)  (Y(2, J), J = 26, 51)
      WRITE(14)  (Y(2, J), J = 52, 77)
      WRITE(14)  (Y(2, J), J = 78, 101)
      WRITE(14)  (Y(2, J), J = 102, 126)
      WRITE(14)  (Y(2, J), J = 127, 152)
      WRITE(14)  (Y(2, J), J = 153, 178)
      WRITE(14)  (Y(2, J), J = 179, 201)
      U(1) = U(2)
      DO  70  J = 1, 201
   70 Y(1, J) = Y(2, J)
      IF  (N.EQ.10)  DLT = 0.1
      IF  (N.EQ.19)  DLT = 1.0
   50 CONTINUE
      END  FILE  14
      REWIND  14
      WRITE(3, 3)  C(M)
    3 FORMAT('1', 10X, 'BETA =', F4.1, /)
      WRITE(3, 4)
    4 FORMAT(3X, '(U)', 6X, 'PLATE(0)', 1X, 'PLATE(0 + N)', 1X,
      'PLATE(1 + N)', 1X, 'PLATE(2 + N)', 1X, 'PLATE(3 + N)',
      1X, 'PLATE(4 + N)', 1X, 'PLATE(5 +N)', 1X, 'PLATE(6 + N)',
      1X, 'PLATE(7 + N)', 1X, 'PLATE(8 + N)', 1X, 'PLATE(9 + N)')
      DO  200  I = 1, L
      READ(14, END = 300)  U1, (Y1(J), J = 1, 25)
      IF  (Y1(2).LT.0.00009)  IX = 1
      READ(14, END = 300) (Y1(J), J = 26, 51)
      READ(14, END = 300) (Y1(J), J = 52, 77)
      READ(14, END = 300) (Y1(J), J = 78, 101)
      READ(14, END = 300) (Y1(J), J = 102, 126)
      READ(14, END = 300) (Y1(J), J = 127, 152)
      READ(14, END = 300) (Y1(J), J = 153, 178)
      READ(14, END = 300) (Y1(J), J = 179, 201)
      WRITE(3, 5)  U1, (Y1(J), J = 1, 11)
    5 FORMAT(//, 1X, F6.2, 2X, 11(F10.4, 1X), 2X)
      IF  (Y1(12).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
      IF     (Y1(12).GT.0.00009)  IX = 0
      WRITE(3, 6)  (Y1(J), J = 12, 21)
      IF  (Y1(22).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
      IF     (Y1(22).GT.0.00009)  IX = 0
      WRITE(3, 6)  (Y1(J), J = 22, 31)
      IF  (Y1(32).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
      IF     (Y1(32).GT.0.00009)  IX = 0
      WRITE(3, 6)  (Y1(J), J = 32, 41)
      IF  (Y1(42).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
      IF     (Y1(42).GT.0.00009)  IX = 0
      WRITE(3, 6)  (Y1(J), J = 42, 51)
      IF  (Y1(52).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
      IF     (Y1(52).GT.0.00009)  IX = 0
```

(continued)

TABLE 1 (continued)

```
          WRITE(3, 6)  (Y1(J), J = 52, 61)
          IF  (Y1(62).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(62).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 62, 71)
          IF  (Y1(72).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(72).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 72, 81)
          IF  (Y1(82).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(82).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 82, 91)
          IF  (Y1(92).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF  (Y1(92).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 92, 101)
          IF  (Y1(102).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(102).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 102, 111)
          IF  (Y1(112).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(112).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 112, 121)
          IF  (Y1(122).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(122).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 122, 131)
          IF  (Y1(132).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(132).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 132, 141)
          IF  (Y1(142).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(142).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 142, 151)
          IF  (Y1(152).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(152).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 152, 161)
          IF  (Y1(162).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(162).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 162, 171)
          IF  (Y1(172).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(172).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 172, 181)
          IF  (Y1(182).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(182).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 182, 191)
          IF  (Y1(192).LT.0.00009.AND.IX.EQ.0)  GO  TO  400
          IF     (Y1(192).GT.0.00009)  IX = 0
          WRITE(3, 6)  (Y1(J), J = 192, 201)
      6   FORMAT(20X, 10(F10.4, 1X), 2X)
    400   CONTINUE
    200   CONTINUE
    300   END  FILE  14
    100   CONTINUE
          STOP
          END
```

TABLE 2

Sample of the Format and Output Data

	$X(n, u)$											
U	$n = 0$	$n = 10r + 1$	$n = 10r + 2$	$n = 10r + 3$	$n = 10r + 4$	$n = 10r + 5$	$n = 10r + 6$	$n = 10r + 7$	$n = 10r + 8$	$n = 10r + 9$	$n = 10r + 10$	$\beta = -0.4$
0.00	0.0	1.0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.01	0.0	0.9836	0.0164	0.0001	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.02	0.0	0.9678	0.0321	0.0003	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.03	0.0	0.9520	0.0473	0.0007	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.04	0.0	0.9368	0.0619	0.0013	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.05	0.0	0.9220	0.0760	0.0020	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.06	0.0	0.9076	0.0896	0.0028	0.0001	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.07	0.0	0.8935	0.1026	0.0038	0.0001	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.08	0.0	0.8798	0.1152	0.0049	0.0001	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.09	0.0	0.8664	0.1274	0.0061	0.0001	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.10	0.0	0.8533	0.1391	0.0074	0.0001	0.0	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.20	0.0	0.7369	0.2348	0.0264	0.0018	0.0001	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.30	0.0	0.6419	0.2996	0.0526	0.0054	0.0004	0.0	0.0	0.0	0.0	0.0	$r = 0$
0.40	0.0	0.5627	0.3418	0.0827	0.0115	0.0012	0.0001	0.0	0.0	0.0	0.0	$r = 0$

0.50	0.0	0.4957	0.3674	0.1139	0.0202	0.0026	0.0003	0.0	0.0	0.0	0.0	$r = 0$
0.60	0.0	0.4383	0.3806	0.1444	0.0312	0.0048	0.0006	0.0001	0.0	0.0	0.0	$r = 0$
0.70	0.0	0.3888	0.3848	0.1727	0.0444	0.0080	0.0011	0.0001	0.0	0.0	0.0	$r = 0$
0.80	0.0	0.3458	0.3824	0.1980	0.0592	0.0122	0.0020	0.0003	0.0	0.0	0.0	$r = 0$
0.90	0.0	0.3085	0.3753	0.2199	0.0751	0.0176	0.0032	0.0005	0.0001	0.0	0.0	$r = 0$
1.00	0.0	0.2753	0.3648	0.2381	0.0917	0.0242	0.0049	0.0008	0.0001	0.0	0.0	$r = 0$
2.00	0.0	0.1061	0.1896	0.2897	0.2105	0.1207	0.0562	0.0200	0.0056	0.0013	0.0002	$r = 0$
3.00	0.0	0.0396	0.1000	0.1883	0.2178	0.1994	0.1273	0.0748	0.0340	0.0130	0.0	$r = 0$
		0.0013	0.0003	0.0001	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$r = 1$
4.00	0.0	0.0148	0.0494	0.1094	0.1618	0.1938	0.1754	0.1333	0.0828	0.0457	0.0206	$r = 0$
		0.0085	0.0031	0.0010	0.0003	0.0001	0.0	0.0	0.0	0.0	0.0	$r = 1$
5.00	0.0	0.0055	0.0232	0.0597	0.1056	0.1499	0.1705	0.1632	0.1296	0.0898	0.0533	$r = 0$
		0.0281	0.0129	0.0055	0.0021	0.0007	0.0002	0.0001	0.0	0.0	0.0	$r = 1$
6.00	0.0	0.0021	0.0105	0.0311	0.0638	0.1035	0.1377	0.1562	0.1509	0.1267	0.0924	$r = 0$
		0.0597	0.0340	0.0176	0.0082	0.0035	0.0014	0.0005	0.0002	0.0001	0.0	$r = 1$
7.00	0.0	0.0008	0.0046	0.0156	0.0364	0.0665	0.1000	0.1289	0.1442	0.1417	0.1224	$r = 0$
		0.0597	0.0640	0.0392	0.0218	0.0111	0.0052	0.0023	0.0009	0.0004	0.0001	$r = 1$
8.00	0.0	0.0003	0.0020	0.0076	0.0198	0.0404	0.0676	0.0968	0.1213	0.1399	0.1336	$r = 0$
		0.1184	0.0940	0.0672	0.0435	0.0257	0.0140	0.0071	0.0033	0.0015	0.0006	$r = 1$
		0.0002	0.0001	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	$r = 2$

TABLE 3

List of Values of the Concentration Parameter y for Different Values of the Volume Parameter u, the Nonlinearity Constant β, and the Plate Number n

$n = 20$						$n = 40$						$n = 60$						$n = 80$					
$\beta = -0.4$		$\beta = 0$		$\beta = 0.5$		$\beta = -0.4$		$\beta = 0$		$\beta = 0.5$		$\beta = -0.4$		$\beta = 0$		$\beta = 0.5$		$\beta = -0.4$		$\beta = 0$		$\beta = 0.5$	
u	y	u	y	u	y	u	y	u	y	u	y	u	y	u	y	u	y	u	y	u	y	u	y
9	.0022	7	.0002	7	.0003	22	.0005	22	.0004	24	.0008	40	.0016	41	.0017	40	.0007	58	.0023	59	.0022	60	.0019
10	.0058	9	.0019	10	.0024	24	.0019	24	.0014	26	.0025	42	.0038	43	.0038	42	.0016	60	.0045	61	.0041	62	.0034
11	.0129	11	.0097	12	.0105	26	.0059	26	.0014	28	.0061	44	.0078	45	.0074	44	.0033	62	.0079	63	.0070	64	.0057
12	.0245	13	.0286	13	.0179	28	.0141	28	.0098	30	.0123	46	.0144	47	.0128	46	.0063	64	.0131	65	.0111	66	.0089
13	.0408	14	.0418	14	.0276	30	.0272	30	.0190	32	.0213	48	.0232	49	.0201	48	.0106	66	.0196	67	.0164	68	.0130
14	.0577	15	.0559	15	.0388	32	.0430	32	.0314	34	.0322	50	.0333	51	.0286	50	.0164	68	.0269	69	.0225	70	.0178
15	.0745	16	.0692	16	.0508	34	.0570	34	.0447	36	.0435	52	.0429	53	.0373	52	.0232	70	.0342	71	.0290	72	.0233
16	.0842	17	.0798	17	.0624	35	.0618	36	.0559	37	.0487	54	.0499	55	.0447	54	.0307	72	.0402	73	.0351	74	.0289
17	.0943	18	.0866	18	.0726	36	.0648	37	.0598	38	.0532	55	.0520	57	.0497	56	.0381	74	.0443	75	.0402	76	.0342
18	.0951	19	.0888	19	.0802	37	.0658	38	.0622	39	.0564	56	.0530	58	.0510	58	.0442	75	.0454	77	.0439	77	.0366
19	.0906	20	.0867	20	.0850	38	.0649	39	.0629	40	.0596	57	.0531	59	.0514	60	.0485	76	.0458	79	.0446	78	.0386
20	.0822	21	.0809	21	.0856	39	.0624	40	.0622	41	.0609	58	.0521	60	.0510	62	.0500	77	.0456	80	.0443	70	.0405
21	.0118	22	.0724	22	.0827	40	.0586	41	.0600	42	.0608	59	.0504	61	.0498	64	.0485	78	.0447	81	.0435	80	.0419
22	.0605	23	.0624	23	.0765	41	.0540	42	.0566	43	.0594	60	.0481	62	.0478	66	.0442	79	.0435	83	.0404	81	.0429
23	.0496	24	.0519	24	.0677	42	.0488	44	.0472	44	.0566	62	.0419	64	.0422	68	.0377	80	.0418	85	.0360	82	.0433
24	.0394	25	.0418	25	.0575	44	.0378	46	.0363	46	.0428	64	.0347	66	.0352	70	.0301	82	.0372	87	.0306	83	.0433
25	.0307	26	.0327	26	.0468	46	.0274	48	.0260	48	.0372	66	.0274	68	.0278	72	.0226	84	.0320	89	.0250	84	.0429
26	.0232	27	.0249	28	.0278	48	.0188	50	.0175	50	.0263	68	.0208	70	.0209	74	.0160	86	.0265	91	.0196	86	.0404
27	.0172	28	.0185	30	.0145	50	.0122	52	.0110	52	.0171	70	.0151	72	.0150	76	.0107	88	.0212	93	.0149	88	.0362
28	.0175	29	.0134	32	.0068	52	.0075	54	.0066	54	.0103	72	.0105	74	.0103	78	.0068	90	.0164	95	.0108	90	.0309
29	.0089	30	.0100	34	.0029	54	.0044	56	.0037	56	.0059	74	.0071	76	.0067	80	.0042	92	.0124	97	.0076	92	.0251
30	.0062	31	.0066	36	.0012	56	.0024	58	.0020	58	.0031	76	.0046	78	.0042	82	.0024	94	.0089	99	.0052	94	.0194
31	.0042	33	.0030	38	.0004	58	.0013	60	.0010	60	.0016	78	.0029	80	.0026	84	.0014	96	.0063	101	.0034	96	.0143
32	.0028	35	.0013	40	.0002	60	.0007	62	.0005	62	.0008	80	.0017	82	.0015	86	.0007	98	.0043	103	.0022	98	.0100
34	.0012	37	.0005	42	.0001	62	.0003	64	.0002	64	.0005	82	.0010	84	.0009	88	.0004	100	.0029	105	.0014	100	.0069

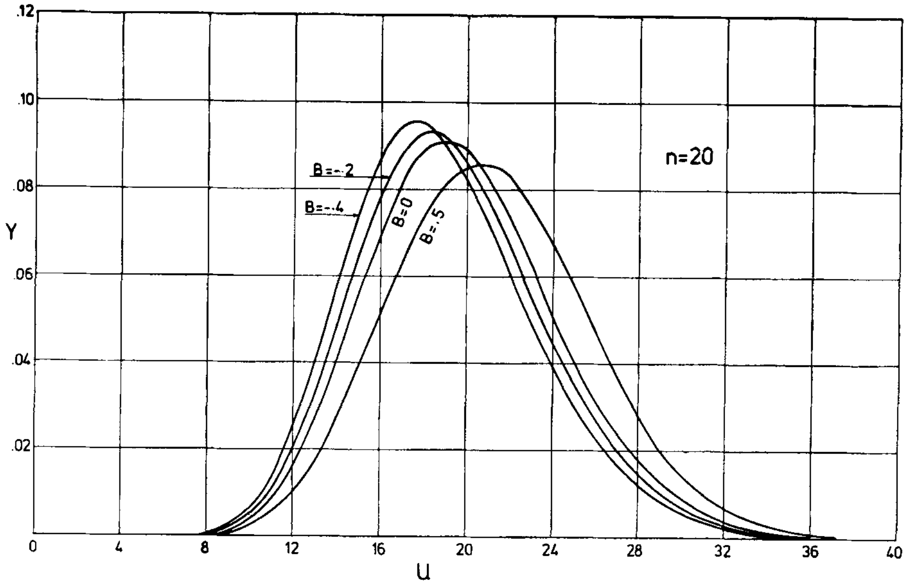


FIG. 1. Elution curve shapes for different values of the nonlinearity factor β, $n = 20$.

it leads to the tabulated Poisson distribution function, in order to check the accuracy of the output data. Figures 1 and 2 are plots of data from Table 3.

THE PRESENT THEORY

The present theory will be mainly concerned with slightly nonlinear isotherms. This might seem to represent a limited number of cases, but at the very low concentrations encountered in chromatography, a large number of separations should belong to this case.

A slightly nonlinear isotherm is not only represented by Eq. (2) but the value of bC_n is also small enough compared to 1 so that

$$x_n = \frac{k_0 C_n}{1 + bC_n} \cong k_0 C_n(1 - bC_n) \tag{12}$$

Considering the movement of the peak along the column as a whole, one deduces that different points of the peak will be moving at different velocities which depend on the concentration. In the usual case where b in Eq. (2) is positive or β in Eq. (3) is negative, the maximum point will be moving at a higher velocity than the center of gravity of the peak which

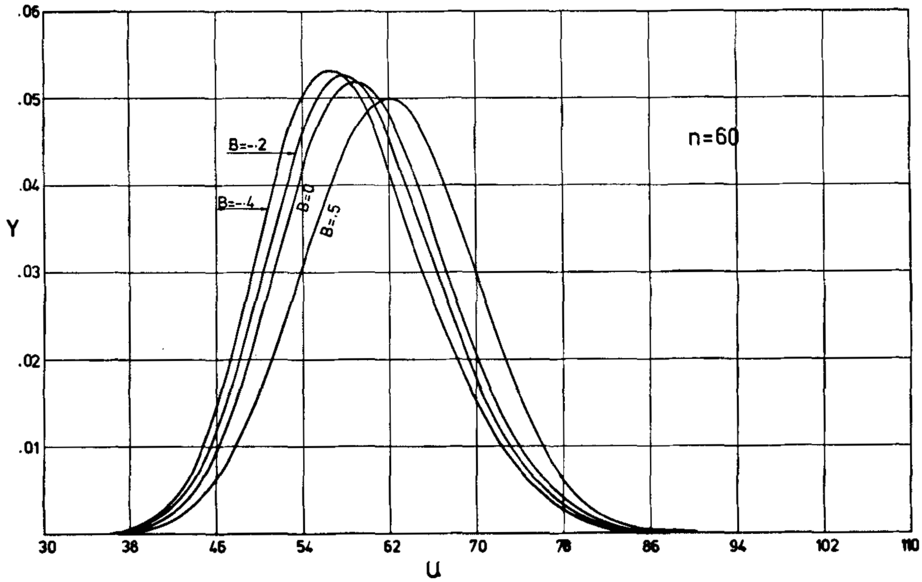


FIG. 2. Elution curve shapes for different values of β, $n = 60$.

in turn will be moving at a velocity higher than the base velocity corresponding to zero concentration. On the other hand, in the not too common cases where b is negative, the maximum point will be moving at a velocity less than that of the center of gravity which moves at a velocity less than the base velocity. It will be shown that as long as $bx_n \ll 1$ and regardless of the value of b, the center of gravity of a chromatographic peak moves at an instantaneous relative velocity (relative to the base velocity) equal to $1/\sqrt{2}$ or 0.7 of the instantaneous relative velocity of the peak maximum.

The velocity u of any point in the peak is related to the velocity of the mobile phase u_a by the relation

$$u = u_a \frac{1}{1 + k}$$

Similarly, for the base velocity u_0:

$$u_0 = u_a \frac{1}{1 + k_0}$$

therefore

$$u = u_0 \frac{1 + k_0}{1 + k}$$

$$k = \frac{k_0}{1 + bC}$$

Applying Eq. (12), one can show that

$$u = u_0\left(1 + \frac{k_0}{1 + k_0} bC\right)$$

or

$$u = u_0(1 - \beta C) \tag{13}$$

where

$$\beta = -\frac{k_0}{1 + k_0} b$$

β in Eq. (13) is essentially the same as β in Eq. (3) except for the difference in plate model.

The velocity of the peak maximum is

$$u_m = u_0(1 - \beta C_m) \tag{14}$$

The velocity of the center of gravity is

$$u_c = \int_{-\infty}^{\infty} (uC)\, dx \Big/ \int_{-\infty}^{\infty} C\, dx \tag{15}$$

Substituting for u from Eq. (13), one gets

$$u_c = u_0 - \beta \frac{\int_{-\infty}^{\infty} C^2\, dx}{\int_{-\infty}^{\infty} C\, dx} \tag{16}$$

but the y coordinate y_c of the center of gravity of a peak is given by

$$y_c = \frac{1}{2} \int_{-\infty}^{\infty} C^2\, dx \Big/ \int_{-\infty}^{\infty} C\, dx \tag{17}$$

leading to

$$u_c = u_0 - 2\beta y_c \tag{18}$$

y_c is the y coordinate of the center of gravity of the peak.

From Eqs. (14) and (18) one gets

$$\frac{u_c - u_0}{u_m - u_0} = 2r_c \tag{19}$$

r_c is the fractional height of the center of gravity of the peak.

$(u_c - u_0)/(u_m - u_0)$ is the ratio between the relative velocities of center of gravity and peak maximum. Table 4 lists values of r_c for different hypothetical peak shapes.

Asymmetry has no effect on the value of r_c as long as the width at any height ratio r is the same as shown in Fig. 3.

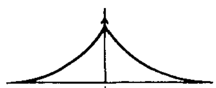
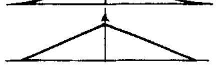
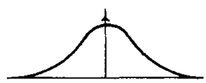
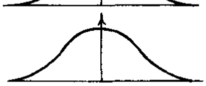
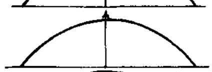
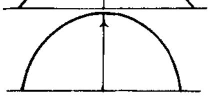
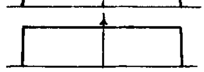
r_c for the Poisson Distribution

Applying Formula (17) on the Poisson distribution,

$$y = e^{-u}\frac{u^n}{n!} \tag{19a}$$

TABLE 4

Values of the Center of Gravity Height Ratio r_c for Different Hypothetical Peak Shapes

Shape Or Formula	Sketch	r_c
e^{-x}		$\frac{1}{4}$ = 0.250
triangle		$\frac{1}{3}$ = 0.333
normal distrbution		$\frac{1}{2\sqrt{2}}$ = 0.354
$\cos^2 x$		$\frac{3}{8}$ = 0.375
$\cos x$		$\frac{\pi}{8}$ = 0.393
$x(1-x)$		$\frac{2}{5}$ = 0.400
half circle		$\frac{4}{3\pi}$ = 0.424
rectangle		$\frac{1}{2}$ = 0.500

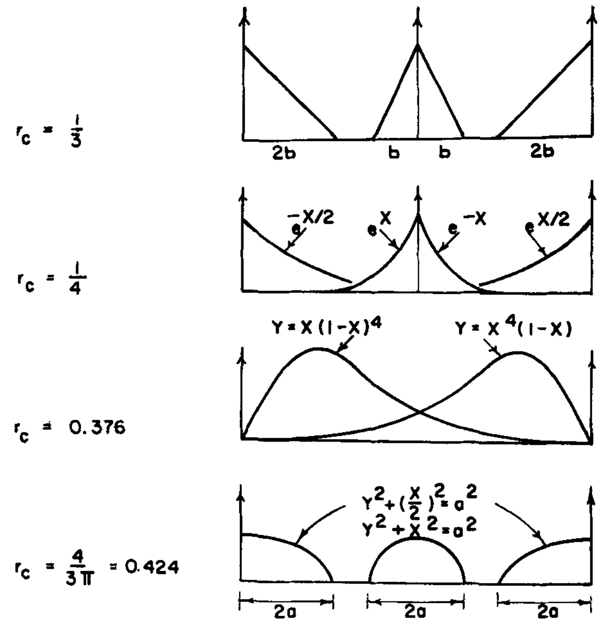


FIG. 3. Some hypothetical peak shapes. Asymmetry has no effect on r_c.

TABLE 5

List of r_c Values for the Poisson Distribution of Different Asymmetries

n	r_c
2	.346
3	.349
4	.350
5	.351
10	.353
∞	.354

it can be shown that

$$r_c = \frac{(2n)!e^n}{2^{2n+2}(n!)n^n} \tag{20}$$

The value of r_c is listed for different values of n in Table 5.

Table 5 shows that r_c for a very asymmetric Poisson distribution ($n = 2$) varies only slightly from r_c for the symmetrical normal distribution ($n = \infty$). One concludes that r_c for asymmetric chromatographic peaks where the asymmetry is due to nonlinearity of the adsorption isotherm is equal to 0.35, in which case Eq. (19) becomes

$$\frac{u_c - u_0}{u_m - u_0} = 0.7 \cong \frac{1}{\sqrt{2}} \tag{21}$$

Peak Retention Time

As the peak moves along the column, the peak maximum C_m decreases and accordingly the velocity of peak maximum and center of gravity must also decrease (for negative β). Integration is needed to calculate t_{rm}, the retention time of peak maximum, so that

$$t_{rm} = \int_0^L \frac{dl}{u_m} \tag{22}$$

Substituting from Eq. (14) gives

$$t_{rm} = \int_0^L \frac{dl}{u_0(1 - \beta C_m)} \tag{23}$$

The relation between C_m at any length l and C_f, the maximum concentration at the column outlet, is known for the case of the linear isotherm and should apply also for the slightly nonlinear isotherm and therefore

$$C_m = C_f\sqrt{\frac{L}{l}} \tag{24}$$

Substituting in Eq. (23) and applying Eq. (12) gives

$$t_{rm} = \int_0^L \frac{dl}{u_0}\left(1 + \beta C_f\sqrt{\frac{L}{l}}\right) = \frac{L}{u_0}(1 + 2\beta C_f)$$

or

$$t_{rm} = t_{rm}{}^0(1 + 2\beta C_f) \tag{25}$$

Similarly for the center of gravity retention time:

$$t_{rc} = t_{rc}{}^0\left(1 + \frac{2}{\sqrt{2}}\beta C_f\right) \tag{26}$$

From Eqs. (25) and (26):

$$\frac{t_{rc}{}^0 - t_{rc}}{t_{rm}{}^0 - t_{rm}} = \frac{1}{\sqrt{2}} \tag{27}$$

From the first and second moments of the Poisson distribution, one can easily show that

$$t_{rc}{}^0 - t_{rm}{}^0 = 1 \tag{28}$$

and that the standard deviation

$$\sigma = \sqrt{n + 1} \tag{29}$$

From Eqs. (27) and (28) one gets

$$t_{rc} - t_{rm} = 1 + \frac{\sqrt{2} - 1}{\sqrt{2}}(t_{rm}{}^0 - t_{rm})$$

or

$$t_{rc} - t_{rm} = 1 + 0.3(t_{rm}{}^0 - t_{rm}) \tag{30}$$

VALIDITY OF THE DERIVED EQUATIONS

To check the validity and accuracy of the derived equations, one compares the results obtained from the derived equations with those obtained from the numerical solution of the exact differential equations. As an example, one might compare the value of t_{rm} obtained numerically with the value calculated from Eq. (25). For values of $N = 20$, 40, 60, and 80, $t_{rm}{}^0$ is equal to 19, 39, 59, and 79, respectively, as can be seen from Table 3 and also as can be deduced theoretically when $\beta = 0$. For $\beta = -0.4$ and $\beta = +0.5$, the values of t_{rm} and C_f must be obtained by interpolation from the data in the same table. In this respect, one makes use of the fact that around the maximum point, a normal or Poisson distribution is approximated quite closely by a parabola leading to the following relations:

$$\frac{x}{h} = \frac{1}{2} - \frac{y_1 - y_2}{(y_1 - y_2) + (y_1 - y_3)} \tag{31}$$

and

$$y_m = y_1 + \frac{x}{h}\left(\frac{y_2 - y_3}{4}\right) \tag{32}$$

y_1, y_2, and y_3 are the three largest ordinates in descending order, h is the constant spacing between the ordinates, and x is the distance between peak maximum y_m and the largest ordinate y_1.

For example, to determine t_{rm} and C_f, for $N = 20$ and $\beta = -0.4$ from data in Table 3, one finds $y_1 = 0.0951$, $y_2 = 0.0943$, $y_3 = 0.0905$. Therefore

$$\frac{x}{h} = \frac{1}{2} - \frac{0.0008}{0.0008 + 0.0046} = 0.35$$

TABLE 6

Comparison between Calculated and Exact Values of the Retention Time t_{rm}

		$\beta = -0.4$			$\beta = +0.5$		
N	t_{rm}^0	C_f	t_{rm} exact	t_{rm} from Eq. (25)	C_f	t_{rm} exact	t_{rm} from Eq. (25)
20	19	0.0954	17.65	17.55	0.0859	20.67	20.63
40	39	0.0658	37.03	36.95	0.0612	41.43	41.39
60	59	0.0533	56.59	56.49	0.0500	62.00	61.95
80	79	0.0458	76.17	76.10	0.0434	82.50	82.43

also

$$y_m = 0.0951 + 0.35\left(\frac{0.0038}{4}\right) = 0.0954$$

and hence

$$t_{rm} = 18 - \frac{x}{h} = 18 - 0.35 = 17.65$$

$$C_f = y_m = 0.0954$$

Table 6 compares values of t_{rm} calculated from Eq. (25) with exact values of t_{rm} obtained by interpolation in Table 3. One finds that the two values do not differ significantly, showing that the assumptions leading to Eq. (25) are satisfactory.

ASYMMETRY OF THE POISSON DISTRIBUTION

Figure 4 is a plot of the Poisson distribution for different values of n. It shows that the asymmetry increases as n decreases. It has been established that the Poisson distribution represents the effluent curve for the linear isotherm, in which case n is the number of theoretical plates which is quite large and therefore the asymmetry is very small.

Figures 1 and 2 show that the effluent curves in the case of the nonlinear isotherm also look like Poisson distributions of different asymmetries, in which case n is a measure of the asymmetry and not a measure of the number of theoretical plates. A convenient measure of the asymmetry of the Poisson distribution is the ratio $(t_{rc} - t_{rm})/\sigma$, where σ is the standard deviation. For the Poisson distribution represented by Eq. (19a), $t_{rc} - t_{rm} = 1$ and $\sigma = \sqrt{n+1}$, and hence the asymmetry A_s is given by

$$A_s = \frac{t_{rc} - t_{rm}}{\sigma} = \frac{1}{\sqrt{n+1}} \tag{33}$$

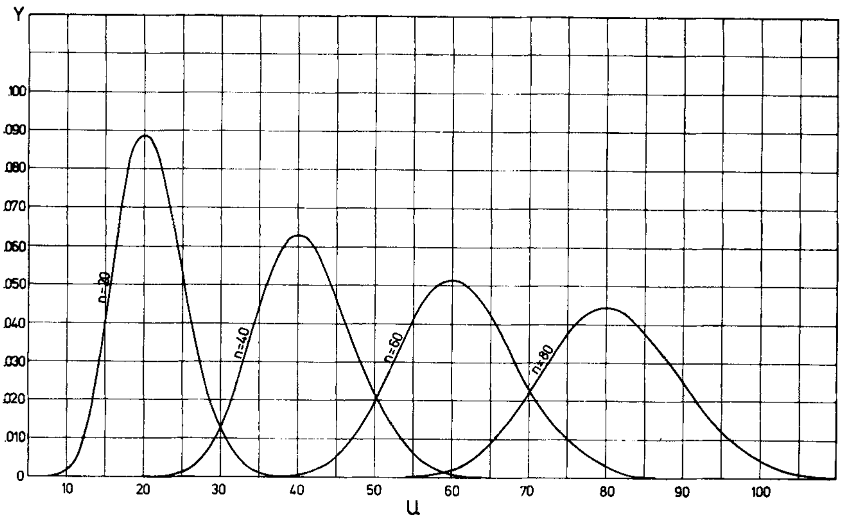


FIG. 4. Plot of the Poisson distribution for different values of n.

FITTING A POISSON DISTRIBUTION TO THE EFFLUENT CURVE OF A NONLINEAR ISOTHERM

The shape of the curves in Figs. 1 and 2 suggests that a negative β leads to more asymmetric Poisson distributions, and in the case of positive β, distributions having asymmetries of the opposite sign are obtained. In other words, the effect of a negative β is to convert the Poisson distribution corresponding to $\beta = 0$ and n equal to the number of theoretical plates to another more asymmetric distribution having a smaller n which is a measure of the asymmetry and not of the number of theoretical plates. If this is true, it would be possible to fit Poisson distributions to computer output data for nonlinear isotherms. For the not too common cases where β is positive, one might fit distributions which are mirror images of the Poisson distribution. Because such cases are very seldom encountered in practice, no effort will be made here to undertake this task.

We will be concerned here with fitting a Poisson distribution to one of the curves tabulated in Table 3; namely, the curve corresponding to $N = 80$ and $\beta = -0.4$. Applying Eq. (30) and using data in Table 5 gives

$$t_{rc} - t_{rm} = 1 + 0.3(79 - 76.17) = 1.85$$

Assuming that the standard deviation of the original distribution did not change much from that for the linear isotherm, then

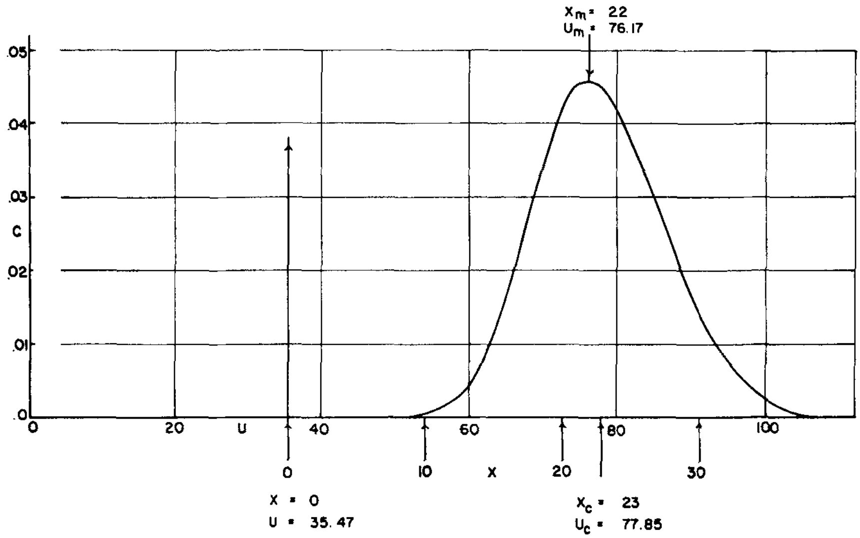


FIG. 5. The Poisson distribution which fits the effiuent curve for $N = 80$, $\beta = -0.4$.

$$\sigma = \sqrt{79 + 1}$$

and the asymmetry of both the original distribution and the fitting distribution is the same so that

$$A_s = \frac{t_{rc} - t_{rm}}{\sigma} = \frac{1.85}{\sqrt{79 + 1}} = \frac{1}{\sqrt{n' + 1}} \tag{34}$$

n' is the value of n for the fitting distribution. The curve of the original distribution is a plot of concentration c vs u as shown in Fig. 5, with the maximum c_f equal to 0.0458 at $u_m = 76.17$

$$C = ae^{-x}\frac{x^{n'}}{n'!} \tag{35}$$

Solving for n' in Eq. (34) gives

$$n' = 22.37$$

If the assumptions made in the derivation of Eq. (25) are valid, it should be possible to fit a Poisson distribution having $n = 22.37$ to the data obtained numerically for $N = 80$ and $\beta = -0.4$. A non- integer value of n is mathematically possible with the application of Stirling's Formula.

$$n! = e^{-n}n^n\sqrt{2\pi n}\left(1 + \frac{1}{12n}\right)$$

For convenience and because the difference is small, a Poisson distribution having $n = 22$ will be fitted to the data. The fitting distribution is therefore represented by the equation

$$c' = ae^{-x}\frac{x^{22}}{22!}$$

with the maximum c_f' equal to 0.0458 at $x_m = 22$. For the sake of comparison, one axis is used for both u and x coordinates as shown in Fig. 5. Since one unit on the x-axis is equal to 1.85 units on the u-axis and both c_f' and x_m are made to coincide with c_f and u_m, then the following relation holds:

$$x = 22 - \frac{76.17 - u}{1.85} \tag{36}$$

because the peak maximum is at $x_m = 22$. Then

$$0.0458 = ae^{-22}\frac{22^{22}}{22!}$$

from which

$$a = 0.5405$$

and the equation for the fitting Poisson distribution becomes

$$C = 0.5405e^{-x}\frac{x^{22}}{22!} \tag{37}$$

Table 7 compares values of C calculated from Eq. (37) with the exact values calculated numerically for $N = 80$ and $\beta = -0.4$. The data are plotted in Fig. 5. The two curves differ only slightly and may be represented practically by one curve as shown in the figure.

CONCLUSION

Nonlinear adsorption isotherms lead to asymmetric effluent curves. When the nonlinearity is slight, the shape of the resulting curves is close to that of a Poisson distribution. Knowing the base capacity ratio k_0, the nonlinearity constant β, and the number of theoretical plates N, it is possible to determine the retention time and effluent curve equation in the form of an asymmetric Poisson distribution.

TABLE 7

Comparison between Calculated and Exact Values of the Concentration Parameter C

u	x	C Exact, for $N = 80$, $\beta = -0.4$	$C = 0.5405e^{-x}(x^{22}/22!)$
58	12.18	0.0023	0.0019
60	13.26	0.0045	0.0042
62	14.34	0.0079	0.0079
64	15.42	0.0131	0.0133
66	16.50	0.0196	0.0200
68	17.58	0.0269	0.0274
70	18.66	0.0342	0.0346
72	19.75	0.0402	0.0405
74	20.83	0.0443	0.0443
76	21.91	0.0458	0.0458
76.17	22.00	0.0458	0.0458
78	22.99	0.0447	0.0448
80	24.07	0.0418	0.0418
82	25.15	0.0372	0.0372
84	26.23	0.0320	0.0320
86	27.31	0.0265	0.0263
88	28.39	0.0212	0.0210
90	29.48	0.0164	0.0162
92	30.56	0.0124	0.0121
94	31.64	0.0089	0.0088
96	32.72	0.0063	0.0063
98	33.80	0.0043	0.0044
100	34.88	0.0029	0.0030

The fact that the tailing of practical peaks may differ from that predicted from a Poisson distribution is due to other factors like overloading, extracolumnar effects, or excessive nonlinearity of the isotherm.

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