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Chemistry Division

ADSORPTION ON MIXTURES OF ION EXCHANGERS

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CONTENTS

	<u>Page</u>
Abstract	1
Introduction	1
Ion Exchange as a Two-Phase Equilibrium	3
Mixed Ion Exchangers	5
Distribution Coefficients in Mixed Ion Exchangers in the Linear Isotherm Region (low loading)	7
Distribution Coefficients in Mixed Ion Exchangers as a Function of Supporting Electrolyte Concentration at Constant m_M	8
Distribution Coefficients for Mixed Exchangers as a Function of m_M at Constant Supporting Electrolyte Concentration	14
Acknowledgements	16
Appendix 1	35
Appendix 2	37

ADSORPTION ON MIXTURES OF ION EXCHANGERS

Roberto Triolo and M. H. Lietzke

ABSTRACT

A theoretical study has been made of adsorption on mixtures of ion exchangers. The effect of variables such as the concentration of the ion being adsorbed, the concentration of the supporting electrolyte, loading, the values of the capacities and equilibrium constants for the various exchange processes, and the fraction of each adsorber in the mixture on the observed distribution coefficient has been investigated. A computer program has been written to facilitate the calculation of distribution coefficients for the adsorption of an ion on a given mixture of ion exchangers under a specified set of conditions.

INTRODUCTION

In the past few years the study of the adsorption of ions on naturally occurring materials, such as clays and other minerals, has received increasing attention because of the initiation of applied programs in areas such as enhanced oil recovery and nuclear waste isolation. In enhanced oil recovery the complex interactions which occur between the micellar floods and the geologic formations containing the oil are to a large extent determined by the ion exchange characteristics both of the formations and of the surfactants used in the process. These interactions must be investigated over a wide range of salinities and of alkali metal to alkaline earth ratios. Work in this area also involves an effort to identify ions which might be used as tracers for underground water flow both under the conditions

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of salinity and alkali metal to alkaline earth ratios encountered in the geologic formations and at the interfaces with the micellar floods. To be a good water tracer an ion should exhibit negligible adsorption under these conditions.

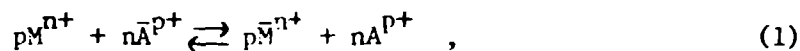
In nuclear waste isolation an important criterion in selection of geological formations as disposal sites for wastes from the nuclear power industry is the degree to which the radioactive substances can be retarded by the storage environment. The retention of these wastes is a function of the adsorption characteristics of the particular minerals involved and of the interaction with ground waters of widely varying compositions which may pass through the formation. Thus work in this area involves the measurement of distribution coefficients for the fission product, actinide, and other ions involved over the range of solution composition which might be encountered in various ground waters, including the highly saline water which could possibly issue from a breach in a salt mine used for waste storage.

The natural formations involved in these applications are complex mixtures. They may contain several substances which can function as adsorbers or ion exchangers. In some cases the minerals may contain very small amounts of impurities which have high adsorption or distribution coefficients for the various (ionic) species encountered. To help appreciate the implications of the behavior of observed distribution coefficients when an ion is adsorbed on a mixed ion exchanger we have written a computer program for calculating the overall distribution coefficient for an ion adsorbed on a mixed exchanger as a function of concentration of the ion being adsorbed, concentration of the supporting

electrolyte, loading, the values of the capacities and equilibrium constants for the various exchange processes, and the fraction of each adsorber in the mixture. In developing the program ideal exchange has been assumed in all cases. By ideal exchange we mean that the value of K/Γ , as defined below, remains constant over the entire range of the computation; that there is no ion-complexing in solution; and that there is no co-ion invasion of the adsorber. Before describing the computer program, however, we will give a description of the properties of mixed ideal ion exchangers.

ION EXCHANGE AS A TWO-PHASE EQUILIBRIUM

Ion exchange is a two-phase equilibrium. The equilibrium for the exchange of an ion M^{n+} with an ion A^{p+} may be represented by



with the corresponding equilibrium constant given by

$$K = \frac{(\bar{m}_M)^p (\bar{m}_A)^n (\bar{\gamma}_M)^p (\bar{\gamma}_A)^n}{(m_M)^p (m_A)^n (\gamma_M)^p (\gamma_A)^n} \quad (2)$$

In these equations the bars refer to concentrations in the adsorber, no bar refers to concentrations in the solution phase, the γ 's are the activity coefficients of the respective species, and \bar{m} represents concentration in moles/liter of solvent or kg of adsorber. The capacity \bar{C} of the adsorber in moles/kg is given by $\bar{C} = p\bar{m}_A + n\bar{m}_M$. Hence $\bar{m}_A = (C - n\bar{m}_M)/p$. If we designate the stoichiometric activity coefficient quotient by Γ and use the foregoing expression for \bar{m}_A in terms

of the capacity of the exchanger, equation (2) becomes

$$\frac{K}{\Gamma} = \frac{(\bar{m}_M)^p (\rho m_A)^n}{(m_M)^p (C - n\bar{m}_M)^n} \quad (3)$$

The stoichiometric activity coefficient quotient Γ is a measurable ratio of the appropriate powers of the mean ionic activity coefficients γ_{\pm} of the electrolytes involved in the exchange reactions. However, in the present discussion the quantity K/Γ is assumed constant for adsorption of an ion on a given exchanger.

It is convenient to speak of the distribution coefficient D_M of the adsorbed ion as defined by $D_M = \bar{m}_M/m_M$. Introducing this into equation (3) and rearranging gives

$$(D_M)^p = \left(\frac{K}{\Gamma}\right) \frac{(C - n\bar{m}_M)^n}{(\rho m_A)^n} \quad (4A)$$

or

$$(D_M) = \left(\frac{K}{\Gamma}\right)^{1/p} \frac{(C - n\bar{m}_M)^{n/p}}{(\rho m_A)^{n/p}} \quad (4B)$$

The term K/Γ is a measure of the relative selectivity of an exchanger for one ion over another. In the following discussion we will focus our attention on the effect of a possibly varying and usually much greater concentration of the ion A^{p+} on the distribution coefficient D_M for the adsorption of an ion M^{m+} .

where the sum is taken over all the individual exchangers in the mixture.

Combining equations (4) and (9) gives the following general expression for the overall distribution coefficient for the adsorption of an ion M^{n+} on a mixed exchanger:

$$D_{\text{observed}} = \frac{1}{(p m_A)^{n/p}} \sum_i F_i \left(\frac{K}{\Gamma} \right)_i^{1/p} (C_i - n \bar{m}_i)^{n/p}. \quad (10)$$

In this equation \bar{m}_i represents the concentration of M in the i^{th} exchanger. For simplicity, in the subsequent development mixed exchangers containing only two components will be considered.

To study the adsorption of an ion in solution on a mixed ion exchanger over a wide range of conditions a computer program has been written. In this program, equation (3) is solved numerically by successive approximations for each exchanger separately to give the value of \bar{m}_M corresponding to fixed values of (K/Γ) , m_M , m_A , C , n , and p . The values of \bar{m}_M obtained in each case are then used to calculate the respective distribution coefficients for the adsorption of the ion in question. Taking into account the fraction of each solid component in the mixed adsorber the value of D_{obs} is then calculated using equation (9). Further details concerning the mathematical methods used in the computer program are given in Appendix 1. This program has been used to carry out the calculations and produce all the figures in this report.

MIXED ION EXCHANGERS

Since we are interested in the properties of mixed exchangers we need an expression for the overall distribution coefficient for the adsorption of an ion on the exchanger in terms of the fractions of each adsorber in the exchanger. To derive such an expression, consider a mixed exchanger containing g_1 kg of exchanger 1 and g_2 kg of exchanger 2. Let \bar{m}_1 be the amount of an adsorbed ion in exchanger 1 and \bar{m}_2 the amount of the same ion in exchanger 2, in each case per kg of adsorber. Then the total amount of the ion adsorbed per kg of adsorber is given by

$$\text{Total adsorbed/kg} = \frac{\bar{m}_1 g_1}{g_1 + g_2} + \frac{\bar{m}_2 g_2}{g_1 + g_2} \quad (5)$$

However, $\frac{g_1}{g_1 + g_2} = F_1$, the weight fraction of exchanger 1, and $\frac{g_2}{g_1 + g_2} = F_2$, the weight fraction of exchanger 2. Hence, equation (5) may be written

$$\text{Total adsorbed/kg} = \bar{m}_1 F_1 + \bar{m}_2 F_2, \quad (6)$$

where $F_1 + F_2 = 1$. Dividing through by \underline{m} , the concentration of the ion in solution gives

$$\frac{\text{Total adsorbed/kg}}{\underline{m}} = \frac{\bar{m}_1 F_1}{\underline{m}} + \frac{\bar{m}_2 F_2}{\underline{m}} \quad (7)$$

Hence,

$$D_{\text{observed}} = F_1 D_1 + F_2 D_2; \quad (8)$$

or in general

$$D_{\text{observed}} = \sum_i F_i D_i, \quad (9)$$

DISTRIBUTION COEFFICIENTS IN MIXED ION EXCHANGERS
IN THE LINEAR ISOTHERM REGION (LOW LOADING)

In considering the adsorption at low loading of an ion on a mixed exchanger containing two adsorbents it is convenient to write equation (10) as

$$D_{\text{obs}} = \frac{1}{(pm_A)^{n/p}} \left[F_1 \left(\frac{K}{\Gamma} \right)_1^{1/p} C_1^{n/p} \left(1 - \frac{\bar{m}_1}{C_1} \right)^{n/p} + F_2 \left(\frac{K}{\Gamma} \right)_2^{1/p} C_2^{n/p} \left(1 - \frac{\bar{m}_2}{C_2} \right)^{n/p} \right]. \quad (11)$$

In this equation the terms $n \frac{\bar{m}_i}{C_i}$ represent the loadings of \underline{M} on the i^{th} exchanger. If we designate the terms $n \frac{\bar{m}_i}{C_i}$ by L_i and the terms $F_i \left(\frac{K}{\Gamma} \right)_i^{1/p} C_i^{n/p}$ by α_i , equation (11) becomes

$$D_{\text{obs}} = \frac{1}{(pm_A)^{n/p}} \left[\alpha_1 (1-L_1)^{n/p} + \alpha_2 (1-L_2)^{n/p} \right] \quad (12)$$

If now L_1 and $L_2 \ll 1$ and the α_i by assumption are constant at fixed values of F_1 and F_2 , then

$$\ln D_{\text{obs}} = - \frac{n}{p} \ln m_A - \frac{n}{p} \ln p + \ln (\alpha_1 + \alpha_2)$$

and

$$\frac{d \ln D_{\text{obs}}}{d \ln m_A} = - \frac{n}{p} \quad (13)$$

Thus, at negligible loading plots of $\log D_{\text{obs}}$ vs $\log m_A$ are parallel and have slopes of $-n/p$, irrespective of the values of F_1 and F_2 . This

is illustrated for 1-1, 2-1, and 3-1 exchange by consideration of the extreme right hand portions of the curves in Figures 2, 4, and 11, which give $\log D_{\text{obs}}$ vs $\log m_A$ at constant m_M . All the curves are parallel as the relative proportions of the two exchangers vary from pure adsorber 2 to pure adsorber 1; since in this case $p=1$ the curves have limiting slopes at low loading (the linear isotherm region) of -1, -2, and -3, respectively, for 1-1, 2-1, and 3-1 exchange.

DISTRIBUTION COEFFICIENTS IN MIXED ION EXCHANGERS AS A FUNCTION
OF SUPPORTING ELECTROLYTE CONCENTRATION AT CONSTANT m_M

In deriving expressions for the limiting values of D_{obs} for mixed exchangers as a function of m_A , it is convenient to carry out the computations at constant m_M . However, we should point out that this does not correspond to a single sequence of experiments where perhaps the initial concentration m_M , but not the equilibrium value, is controlled. Modeling this more realistic case could be achieved by constructing a family of curves of the type to be described for a range of values of m_M which cover the experimental conditions.

For convenience, we shall derive the expressions for the distribution coefficients in mixed exchangers with the value of p in equation (3) taken as unity. Hence the expressions will apply to 1-1, 2-1, and 3-1 exchange. For completeness, however, an expression will be given for the general case where p may differ from unity.

With p taken as unity, rearrangement of equation (3) gives for each solid

$$\left(\frac{K}{\Gamma}\right) \frac{(m_M)}{(m_A)^n} \left[C - n\bar{m}_M \right]^n - (\bar{m}_M) = 0. \quad (14)$$

We now consider separately the cases where $n = 1$; $n = 2$; and $n = 3$.

(a) With $n = 1$ further rearrangement of (14) gives

$$\left(\frac{K}{1}\right) \frac{(m_M)}{(m_A)} C = \bar{m}_M \left[1 + \left(\frac{K}{1}\right) \frac{(m_M)}{(m_A)} \right] \quad (15)$$

Then,

$$D_{\text{obs}} = \frac{(\bar{m}_M)}{(m_M)} = \frac{\left(\frac{K}{1}\right) C}{m_A \left[1 + \left(\frac{K}{1}\right) \frac{(m_M)}{(m_A)} \right]} = \frac{\left(\frac{K}{1}\right) C}{(m_A) + \left(\frac{K}{1}\right) (m_M)} \quad (16)$$

Now, if we let $m_A \rightarrow 0$ at constant m_M , $D_{\text{obs}} \rightarrow \frac{C}{m_M}$, the maximum value of the distribution coefficient for ideal 1-1 exchange at constant m_M .

When D_{obs} reaches this value the adsorber is fully loaded. In view of equation (9), for 1-1 exchange on a mixed adsorber containing i components

$$D_{\text{obs}} \rightarrow \sum_i F_i \frac{C_i}{m_M} \quad (17)$$

as $m_A \rightarrow 0$ at constant m_M . Since the terms on the right hand side of equation (17) are constant,

$$\left[\frac{d \ln D_{\text{obs}}}{d \ln m_A} \right]_{m_M} = 0 \quad (18)$$

under these conditions. Thus plots of $\log D_{\text{obs}}$ vs $\log m_A$ will approach the ordinate axis at very low m_A with zero slope. The numerical value of D_{obs} in all cases will be given by equation (17).

Consider a mixed exchanger consisting of two adsorbers each with the same ion exchange capacity ($C_1 = C_2 = C$). According to equation (17) the limiting value of D_{obs} at constant m_M will be given by $D_{obs} = C/m_M$ for all relative proportions of the two exchangers. In Figure 1 is shown a plot of $\log D_{obs}$ vs $\log m_A$ for 1-1 exchange of an ion on a mixed adsorber with the following characteristics: $C_1=C_2=1.0$; $(K/\Gamma)_1 = 1.0$; $(K/\Gamma)_2 = 10^4$. With $m_M = 10^{-4}$ moles/liter the limiting value of D_{obs} is given by $1/1 \times 10^{-4} = 10^4$ for all relative proportions of the two exchangers. As shown in the figure, all the curves converge to a single line which approaches the ordinate axis with zero slope. The limiting value of D_{obs} is 10^4 .

If the values of C_i for the two adsorbers are different, then, as the relative proportions of the two adsorbers vary, the limiting values of D_{obs} at low m_A will also vary, but in all cases will be given by equation (17). This is illustrated for 1-1 exchange by the left hand portions of the curves in Figure 2. In this case an ion at $m_M = 10^{-5}$ is adsorbed on a mixed exchanger with $C_1 = 0.1$, $C_2 = 1.0$, $(K/\Gamma)_1 = 1.0$, and $(K/\Gamma)_2 = 10^3$. Application of equation (17) to a mixture containing 50% of each of these components gives a limiting value for D_{obs} of 55,000, the value shown on the plot for this mixture.

(b) Putting $n = 2$ into equation (14) results in a quadratic expression that may be solved using the quadratic formula. The expression for D_{obs} becomes

$$D_{obs} = \frac{4 \left(\frac{K}{\Gamma} \right) m_M C + m_A^2 - \sqrt{8 \left(\frac{K}{\Gamma} \right) m_M C m_A^2 + m_A^4}}{8 \left(\frac{K}{\Gamma} \right) m_M^2} \quad (19)$$

Although the quadratic equation has two roots it can readily be shown by substituting numbers into the equation that adding the radical term in the numerator of equation (19) leads to meaningless values of D_{obs} . If we let $m_A \rightarrow 0$ at constant m_M , $D_{\text{obs}} \rightarrow \frac{1}{2} \frac{C}{m_M}$, and equation (18) again describes the variation of $\log D_{\text{obs}}$ with $\log m_A$ at very low values of m_A . For a mixed exchanger containing i components the limiting expression for D_{obs} at very low values of m_A in the case of 2-1 exchange is

$$D_{\text{obs}} = \frac{1}{2} \sum_i F_i \frac{C_i}{m_M} \quad (20)$$

at constant m_M .

If we consider a mixed exchanger consisting of two components each with the same ion exchange capacity ($C_1 = C_2 = C$) then the limiting value of D_{obs} at constant m_M for 2-1 exchange will be given by $D_{\text{obs}} = \frac{1}{2} \frac{C}{m_M}$ for all relative proportions of the two exchangers. This is illustrated by the left hand portion of the $\log D_{\text{obs}}$ vs $\log m_A$ plot in Figure 4. In this case an ion at a concentration of 10^{-4} moles/l is adsorbed on a mixed exchanger in which both adsorbers have the same capacity ($C_1 = C_2 = 1$) but different K/Γ values: $(K/\Gamma)_1 = 1.0$, $(K/\Gamma)_2 = 100$. Under these conditions the limiting value of D_{obs} is given by $D_{\text{obs}} = \frac{1}{2} 1.0 \times 10^4 = 5000$ for all relative proportions of the two exchangers. If however, the ion exchange capacities of the two adsorbers are different, then as the relative proportions of the two adsorbers vary, the limiting values of D_{obs} at low m_A are all different and are given by equation (20). This is illustrated by considering the left hand portions of the curves shown in Figure 8. Here an ion at

concentration $m_M = 10^{-5}$ is adsorbed on a mixed exchanger in which the adsorbers 1 and 2 have capacities $C_1 = 0.1$ and $C_2 = 1.0$, while $(K/\Gamma)_1 = 50$ and $(K/\Gamma)_2 = 10^4$. In this case the limiting values of D_{obs} vary from 5000 for adsorption on pure component 1 to 50,000 for adsorption on pure component 2.

(c) Putting $n=3$ into equation (14) gives a cubic equation which is difficult to solve explicitly for the three roots corresponding to possible values of \bar{m}_M . However, by substituting reasonable values of (K/Γ) , C , and m_M into the cubic expression and letting $m_A \rightarrow 0$ it can be shown that under these conditions there is only one real root. In solving for this root numerically the same value for \bar{m}_M is obtained regardless of whether the starting estimates are higher or lower than the converged value. Using this value of \bar{m}_M , the limiting value of $D_{obs} \rightarrow \frac{1}{3} \frac{C}{\bar{m}_M}$ in all cases as $m_A \rightarrow 0$. Hence for 3-1 exchange of a trivalent ion on a mixed adsorber at very low values of m_A

$$D_{obs} = \frac{1}{3} \sum_i F_i \frac{C_i}{\bar{m}_M} \quad (21)$$

Figures 11 and 12 illustrate plots of $\log D_{obs}$ vs $\log m_A$ for 3-1 exchange on a mixed adsorber under conditions where the capacities of the two exchangers are the same and where the capacities are different. In all cases the limiting values of D_{obs} at very low values of m_A are given by equation (21).

(d) $n - p$ Exchange on a Mixed Adsorber. In the general case of $n - p$ exchange on a mixed adsorber it is easy to show that as $m_A \rightarrow 0$ at constant m_M the limiting value of D_{obs} becomes

$$D_{\text{obs}} \rightarrow \frac{1}{n} \sum_i F_i \frac{C_i}{m_M} \quad (22)$$

We have discussed the behavior of the overall distribution coefficient for the adsorption of an ion at fixed concentration in solution on a mixed ion exchanger, both at low loading, which occurs at high values of m_A , and at high loading, which occurs at low values of m_A . In the intermediate range the behavior of the overall distribution coefficient is strongly influenced by the relative values of K/Γ for the various components in the mixed exchanger. This is illustrated in Figures 4 through 7 for adsorption of a divalent ion at $m_M = 1 \times 10^{-4}$ on a mixed adsorber in which both solid components have a capacity of 1. With $(K/\Gamma)_2$ equal to 100 and $(K/\Gamma)_1$ equal to 1 there is a slight suggestion of a change of slope in the plot for the mixture containing 5% of component 2. As the value of $(K/\Gamma)_2$ increases from 100 to 100,000 with $(K/\Gamma)_1$ fixed at 1, this effect becomes much more pronounced because the second adsorber becomes loaded much more quickly than does the first. This behavior observed in plots of $\log D_{\text{obs}}$ vs $\log m_A$ is indicative of a mixed adsorber. However, in many cases, especially when the (K/Γ) values for the components in a mixed exchanger are not too dissimilar, the effect may hardly be noticeable, as in Figure 4. This is also the case for the $\log D_{\text{obs}}$ vs $\log m_A$ plots shown for 1-1 exchange in Figures 2 and 3. As will be shown later, a far better method for differentiating a mixture from a "pure" adsorber is to determine $\log D_{\text{obs}}$ vs loading of the adsorber at constant m_A .

The presence in a mixed exchanger of even a very small amount of an adsorber having a high value of K/Γ relative to the value of K/Γ for the adsorber present as the major component may have a dramatic effect on the value of D_{obs} for the adsorption of an ion even at trace loading. This is illustrated in Figure 7 for the adsorption of a divalent ion at $m_M = 1 \times 10^{-4}$ on a mixed exchanger in which both adsorbers have the same capacity $C=1$ but different K/Γ values: $(K/\Gamma)_2 = 100,000$, $(K/\Gamma)_1 = 1$. Note that the presence of only 0.1% of component 2 in the mixture increases the value of D_{obs} by a factor of 40, at a supporting electrolyte concentration of 4.5 m, over the value observed for adsorption on pure component 1. Thus, supposedly pure samples of a clay from different sources may exhibit different values of D_{obs} for the adsorption of a particular ion due to the presence in the samples of differing small amounts of impurities with high distribution coefficients.

In Figures 9 and 10 are shown $\log D_{obs}$ vs $\log m_A$ plots for 2-1 exchange on a mixed adsorber at two different values of m_M . The values of m_A (.02 to 4.5 m) in these plots span a range commonly encountered in experimental situations. Here again the strong effect on D_{obs} of small amounts of a component with a large value of K/Γ in a mixture is illustrated.

DISTRIBUTION COEFFICIENTS FOR MIXED EXCHANGERS AS A FUNCTION OF m_M AT CONSTANT SUPPORTING ELECTROLYTE CONCENTRATION

We pointed out in the previous section that distribution coefficients are not experimentally measured at constant values of m_M . However, it is relatively easy under most conditions to measure distribution coefficients as a function of m_M at constant values of m_A , the supporting

electrolyte concentration.

In an ion exchange equilibrium, as the concentration in solution of the ion adsorbed $m_M \rightarrow 0$ at constant m_A , the concentration of the ion in the adsorber \bar{m}_M also approaches zero. Hence, the term $(C - n\bar{m}_M)^n$ in equation (6) approaches the ion exchange capacity \underline{C} and

$$D_M \rightarrow \left(\frac{K}{\Gamma}\right)^{1/p} \left(\frac{C}{pm_A}\right)^{n/p} \quad (23)$$

For a mixed adsorber the corresponding limiting value of D_{obs} as $m_M \rightarrow 0$ at constant m_A is thus given by

$$D_{obs} = \sum_i F_i D_i = \frac{1}{(pm_A)^{n/p}} \sum_i F_i \left(\frac{K}{\Gamma}\right)_i^{1/p} C_i^{n/p} \quad (24)$$

Figure 13 shows plots of $\log D_{obs}$ vs $\log m_M$ for 1-1 exchange on a mixed adsorber with $C_1 = C_2 = 1$, $(K/\Gamma)_1 = 1$, and $(K/\Gamma)_2 = 100$. With m_A equal to 0.1 the limiting value of D_{obs} as $m_M \rightarrow 0$ for a mixture containing 0.5 weight fraction of each component is 505 as computed using equation (24). This is the value shown on the plot. As the value of m_M increases the values of D_{obs} begin to decrease and eventually go down with a slope of minus one. Note that only the curves for the mixtures with the three lowest weight fractions of the second component show slight inflexions indicative of a mixed adsorber. A much more dramatic way to differentiate between a "pure" adsorber and a mixed adsorber is to plot $\log D_{obs}$ vs loading of the adsorber at fixed values of m_A . Figure 14 shows the loading plots for 1-1 adsorption on a mixed exchanger under the same conditions as those for the $\log D_{obs}$ vs $\log m_M$ plots

shown in Figure 13. Of course, the limiting values of D_{obs} (corresponding to zero loading) are the same in both Figures 13 and 14 and the values of D_{obs} eventually all approach a limiting value at full loading of both adsorbers. However, in the intermediate regions the overall "observed" values of D for the mixed adsorbers much more clearly reflect the composite nature of the adsorber. Similar plots for 2-1 and 3-1 exchange on mixed exchangers are shown in Figures 15 - 18.

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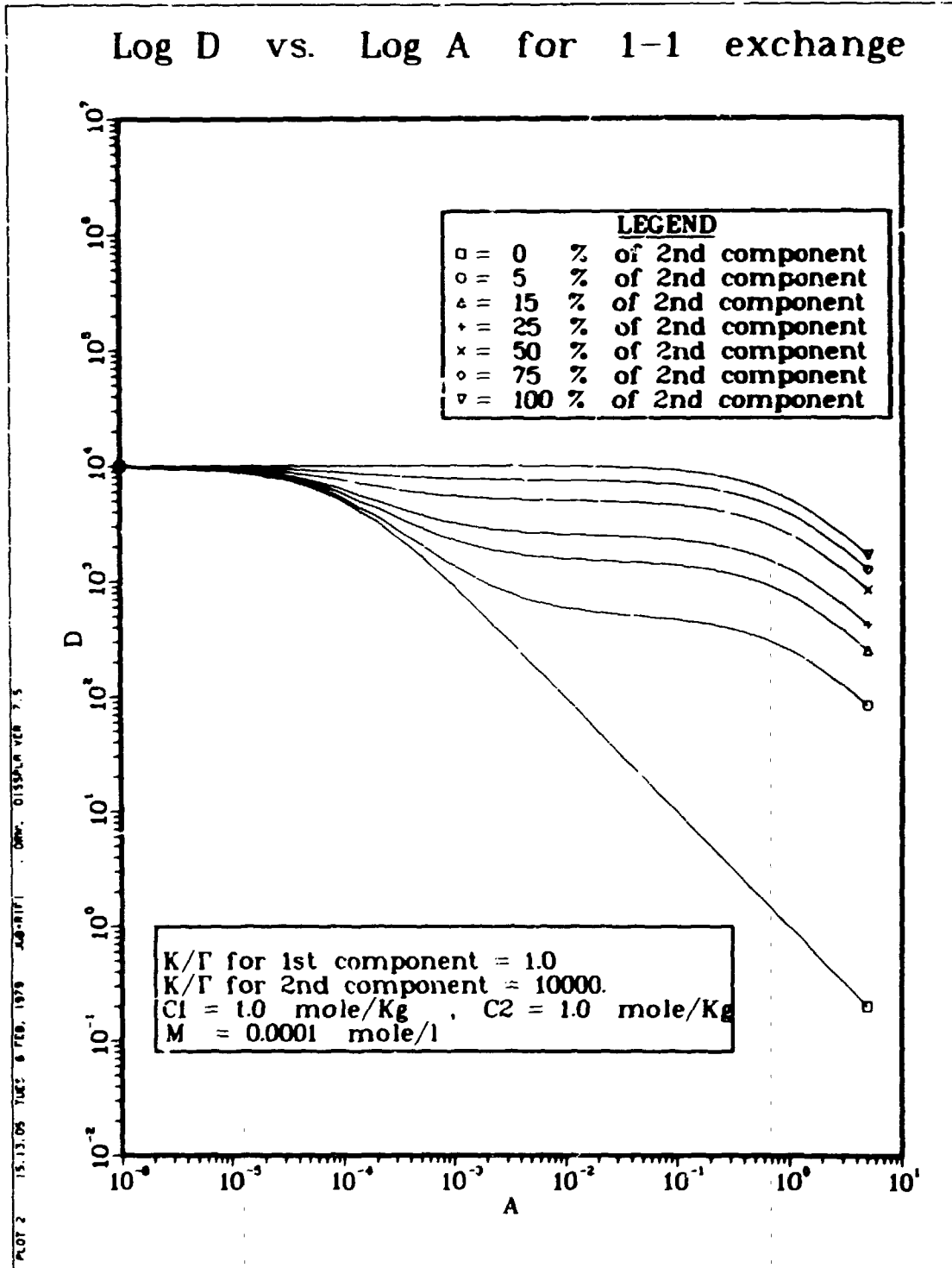


Figure 1

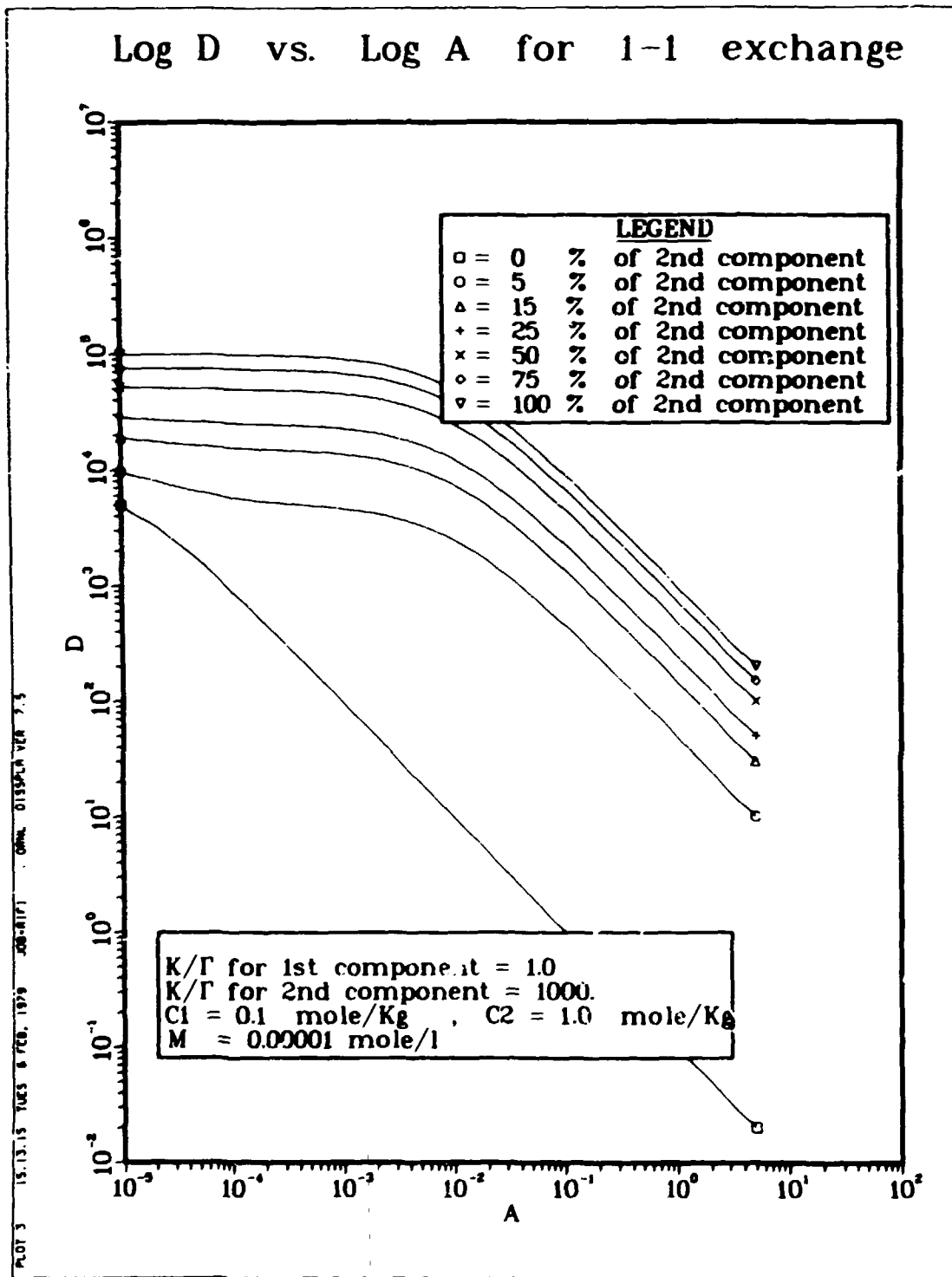


Figure 2

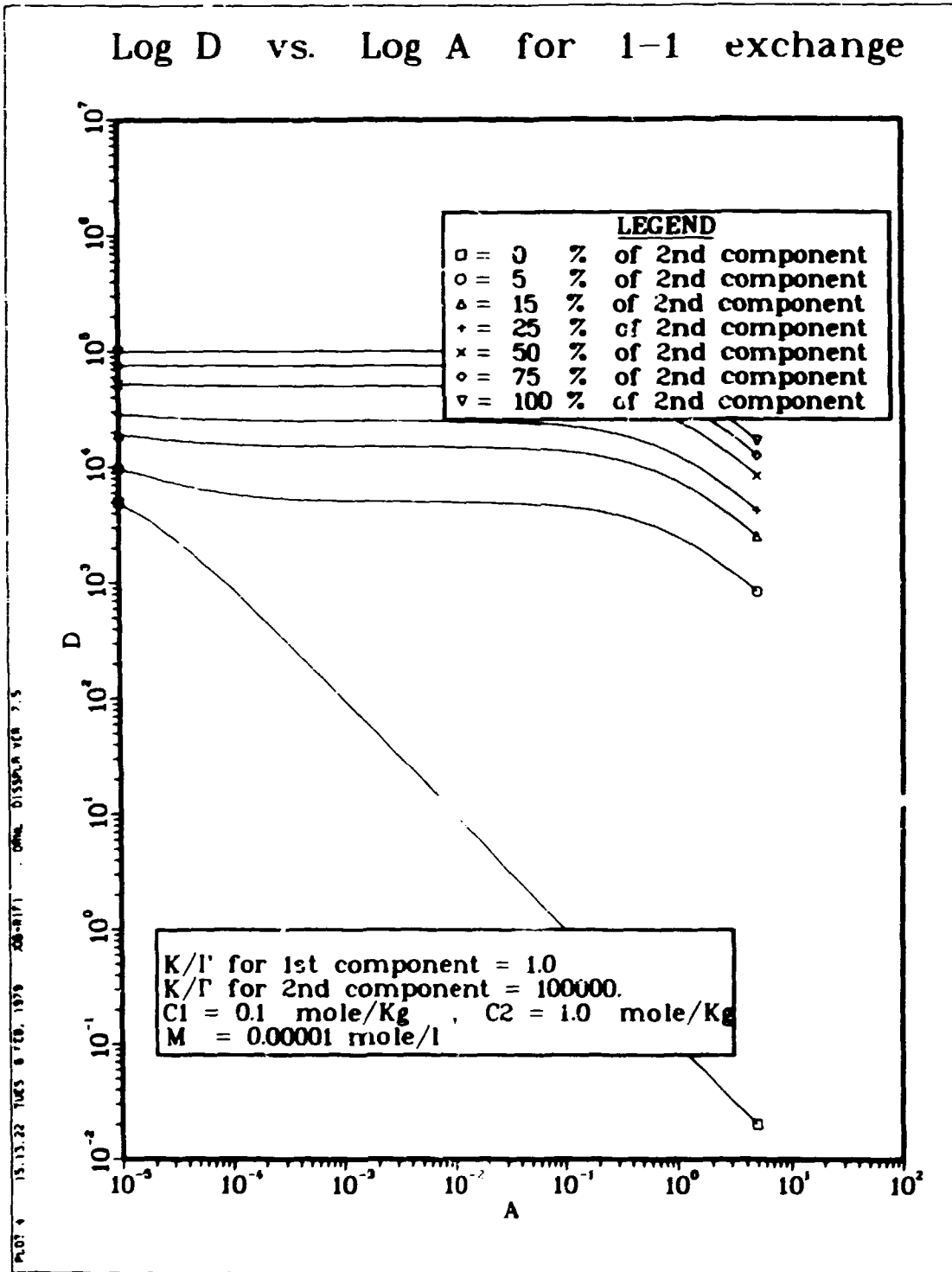


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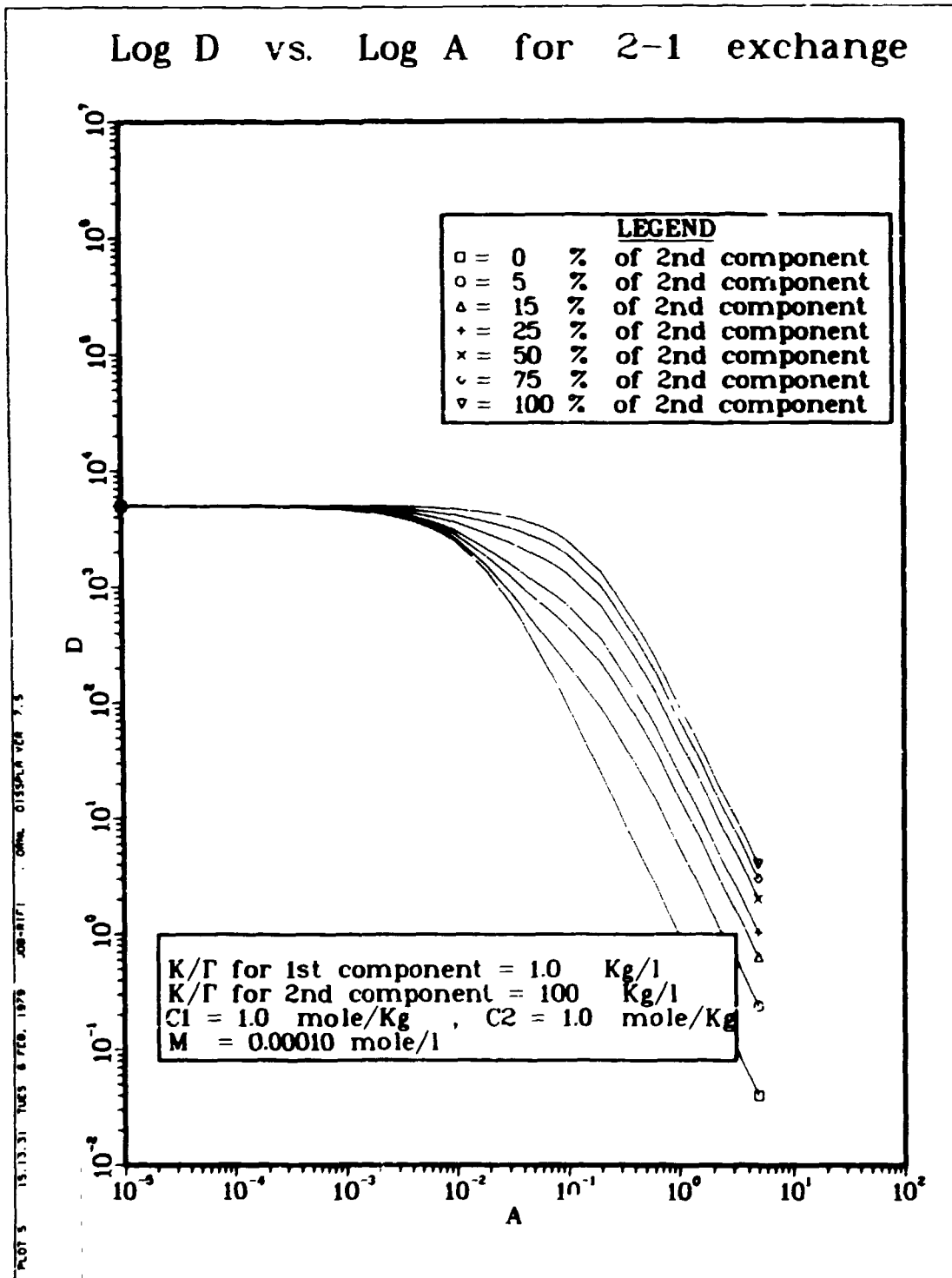


Figure 4

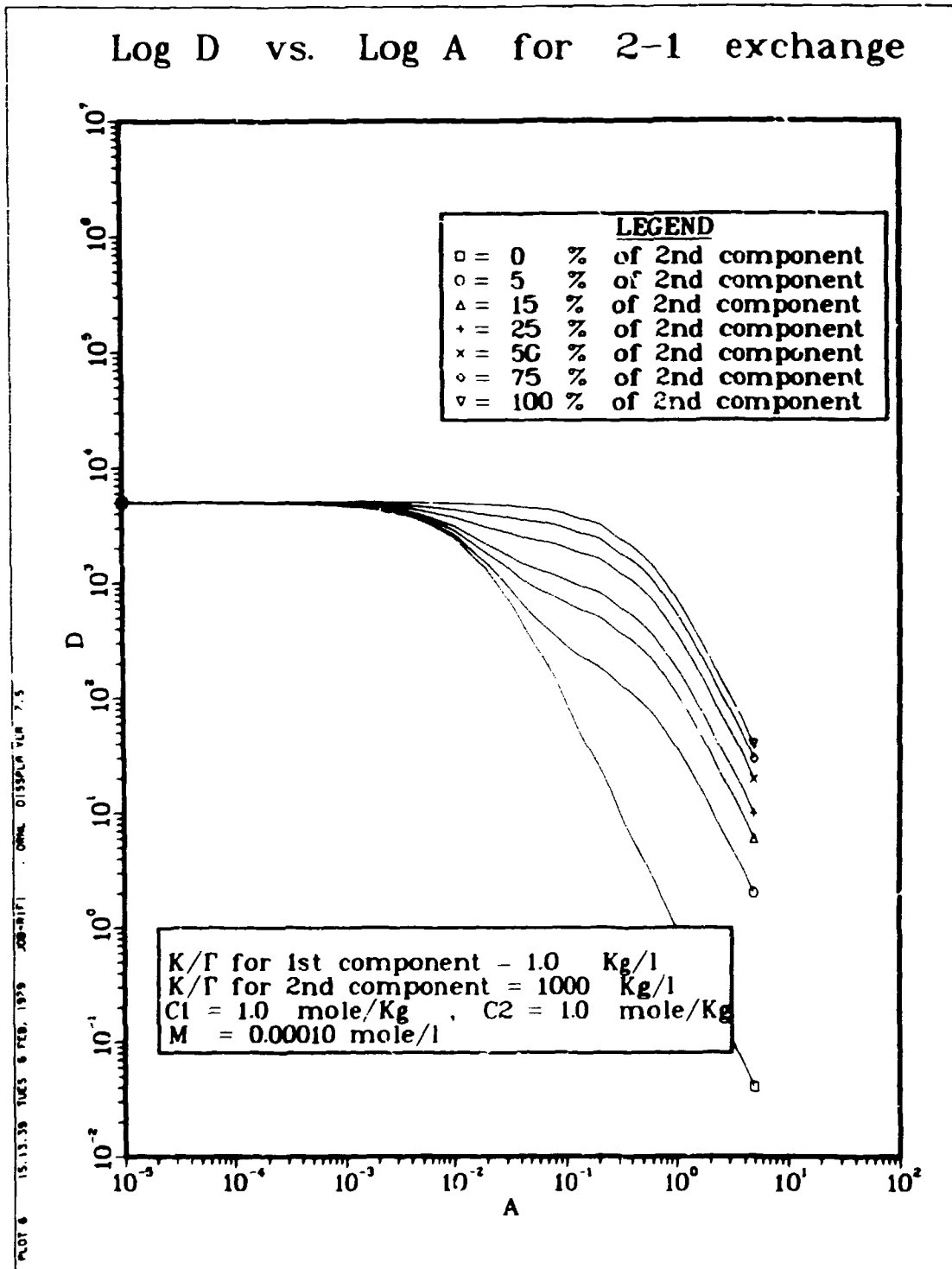


Figure 5

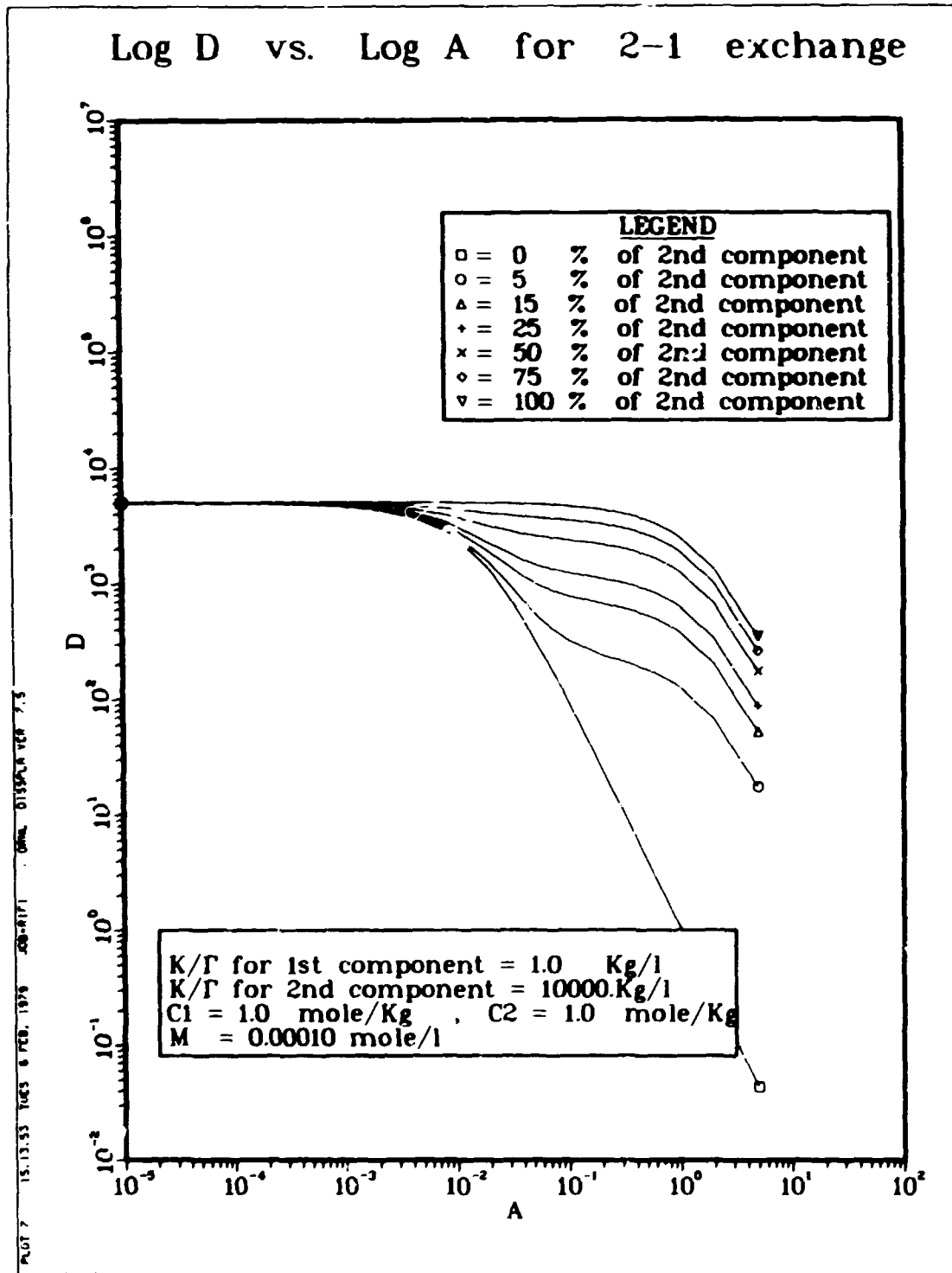


Figure 6

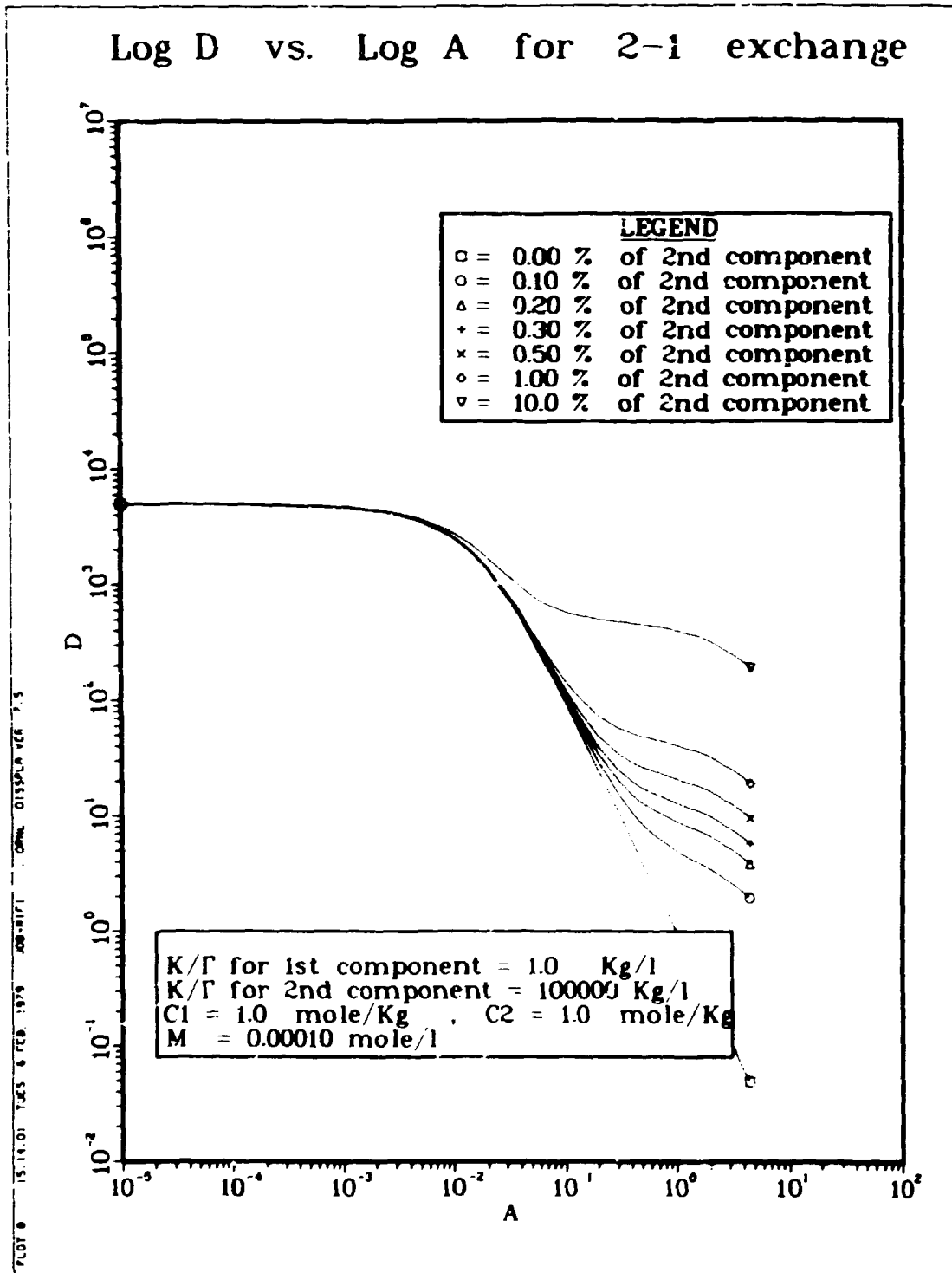


Figure 7

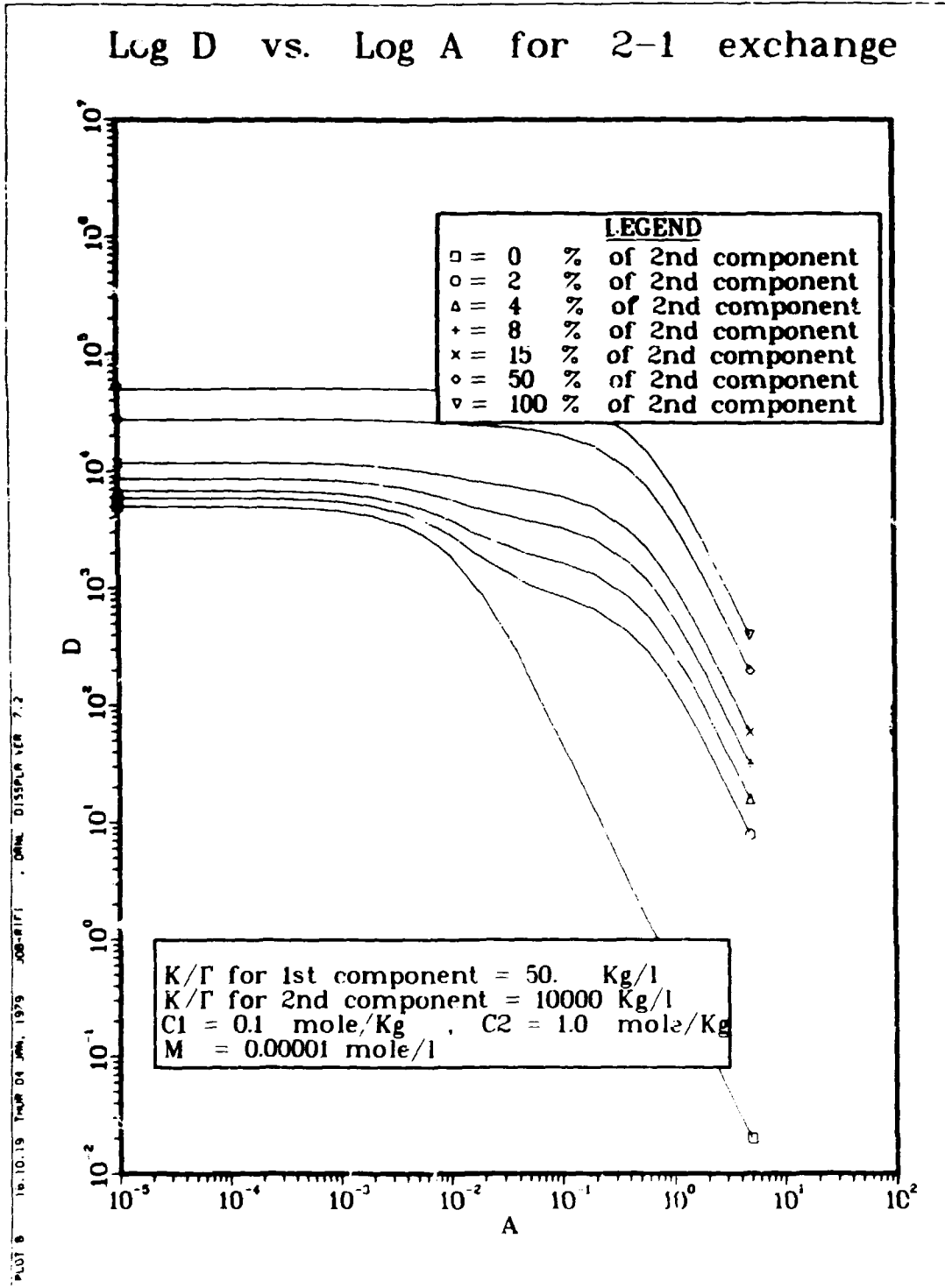
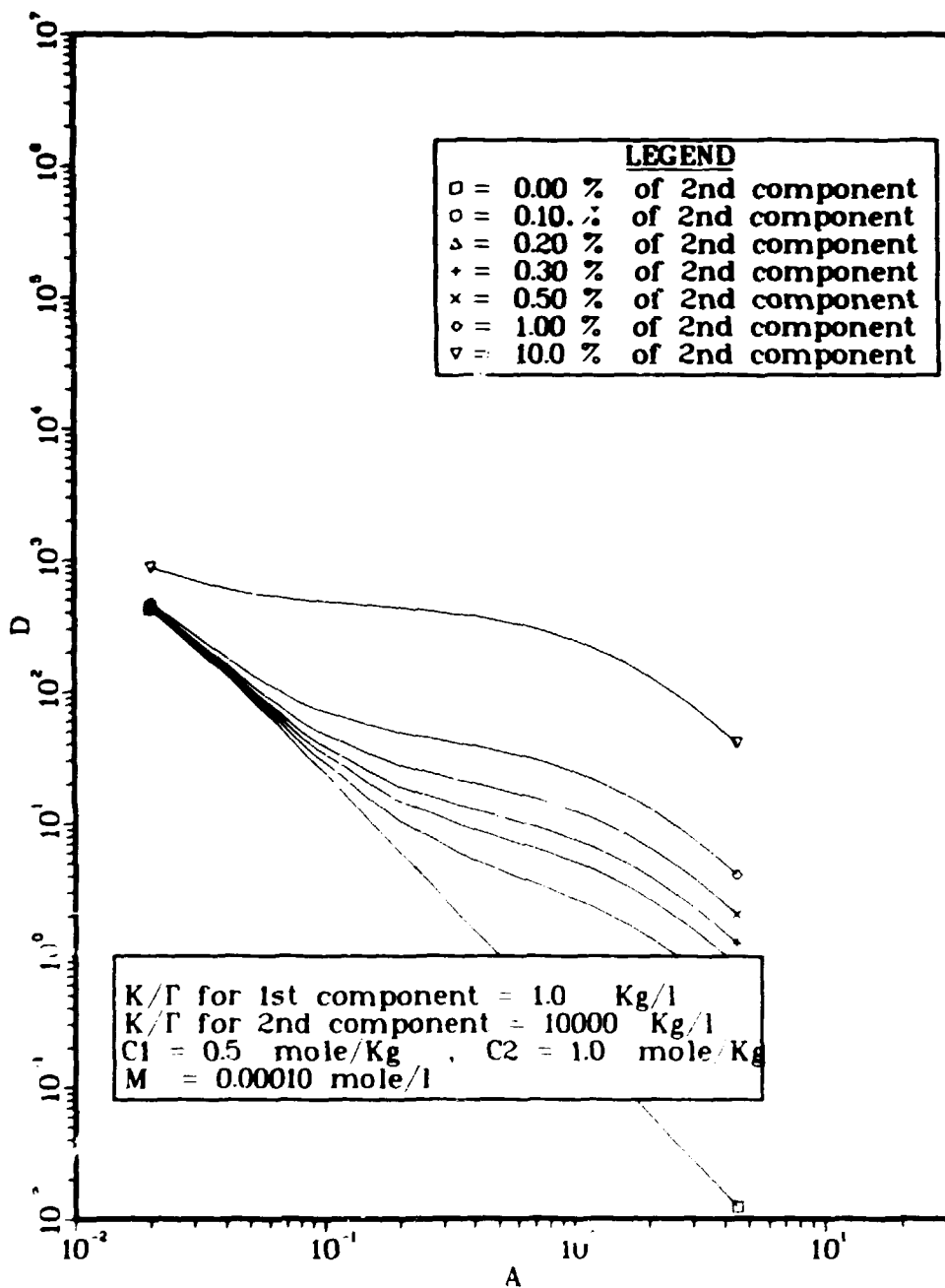


Figure 8

Log D vs. Log A for 2-1 exchange



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Figure 9

Log D vs. Log A for 2-1 exchange

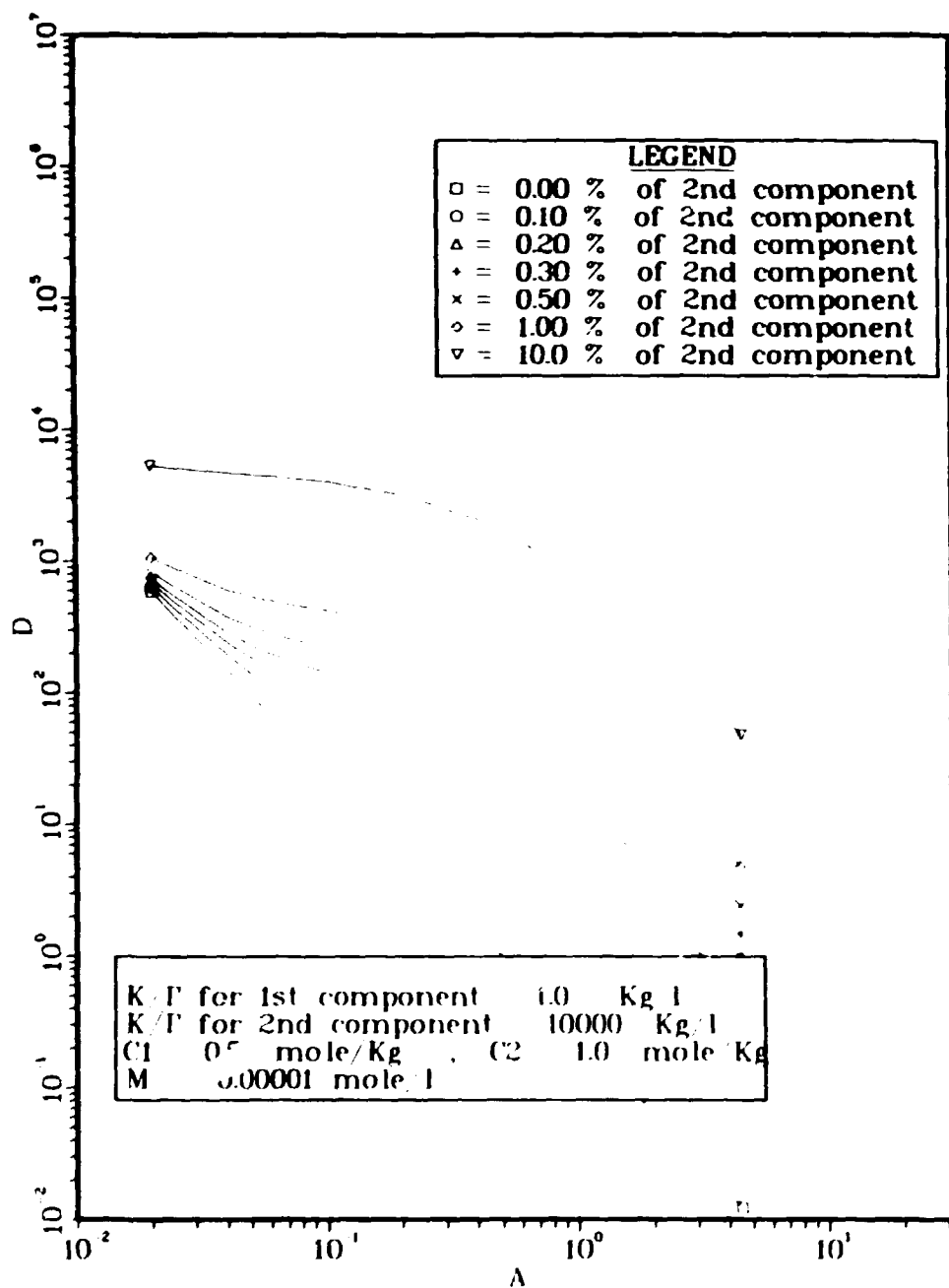


Figure 10

Log D vs. Log A for 3-1 exchange

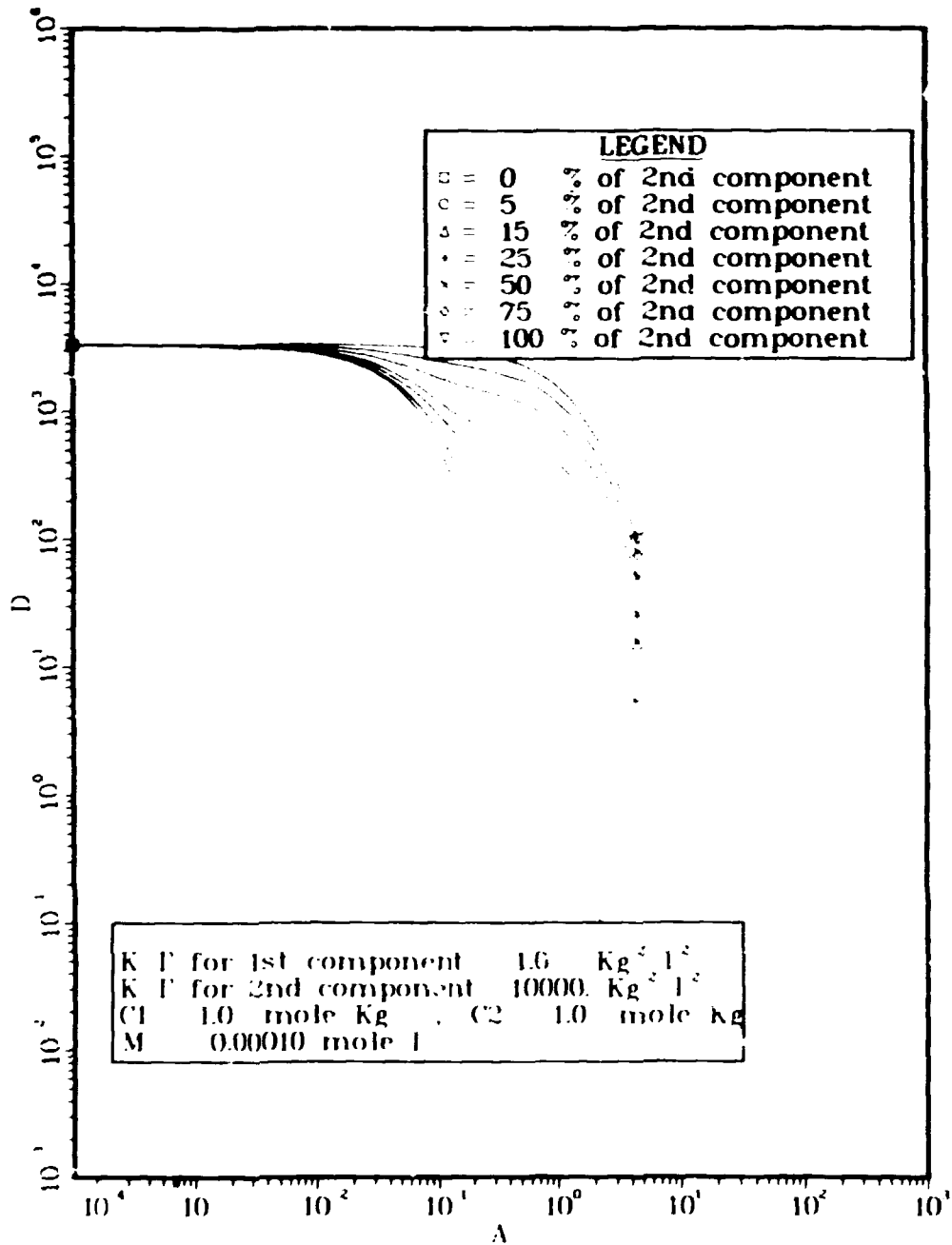


Figure 11

Log D vs. Log A for 3-1 exchange

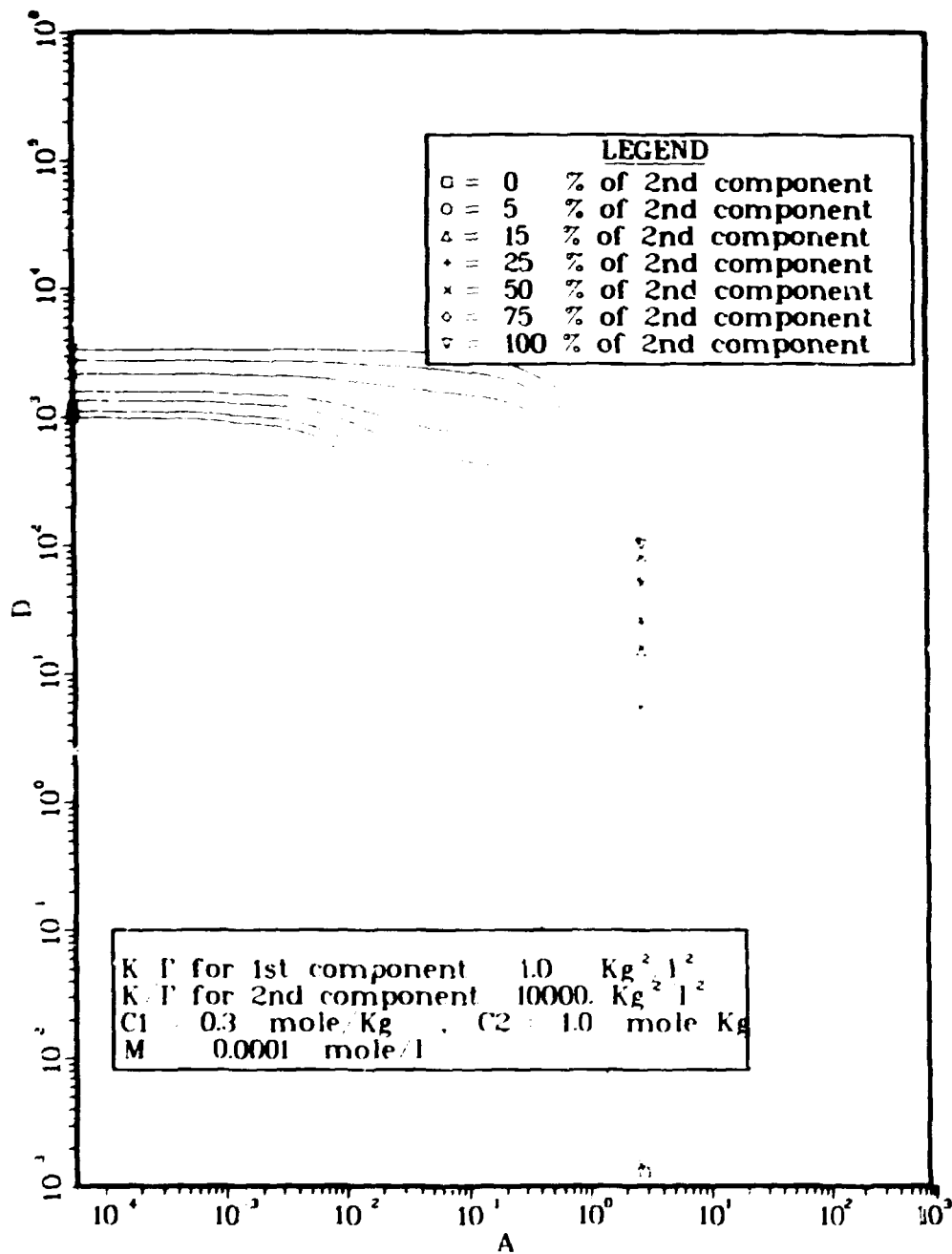


Figure 12

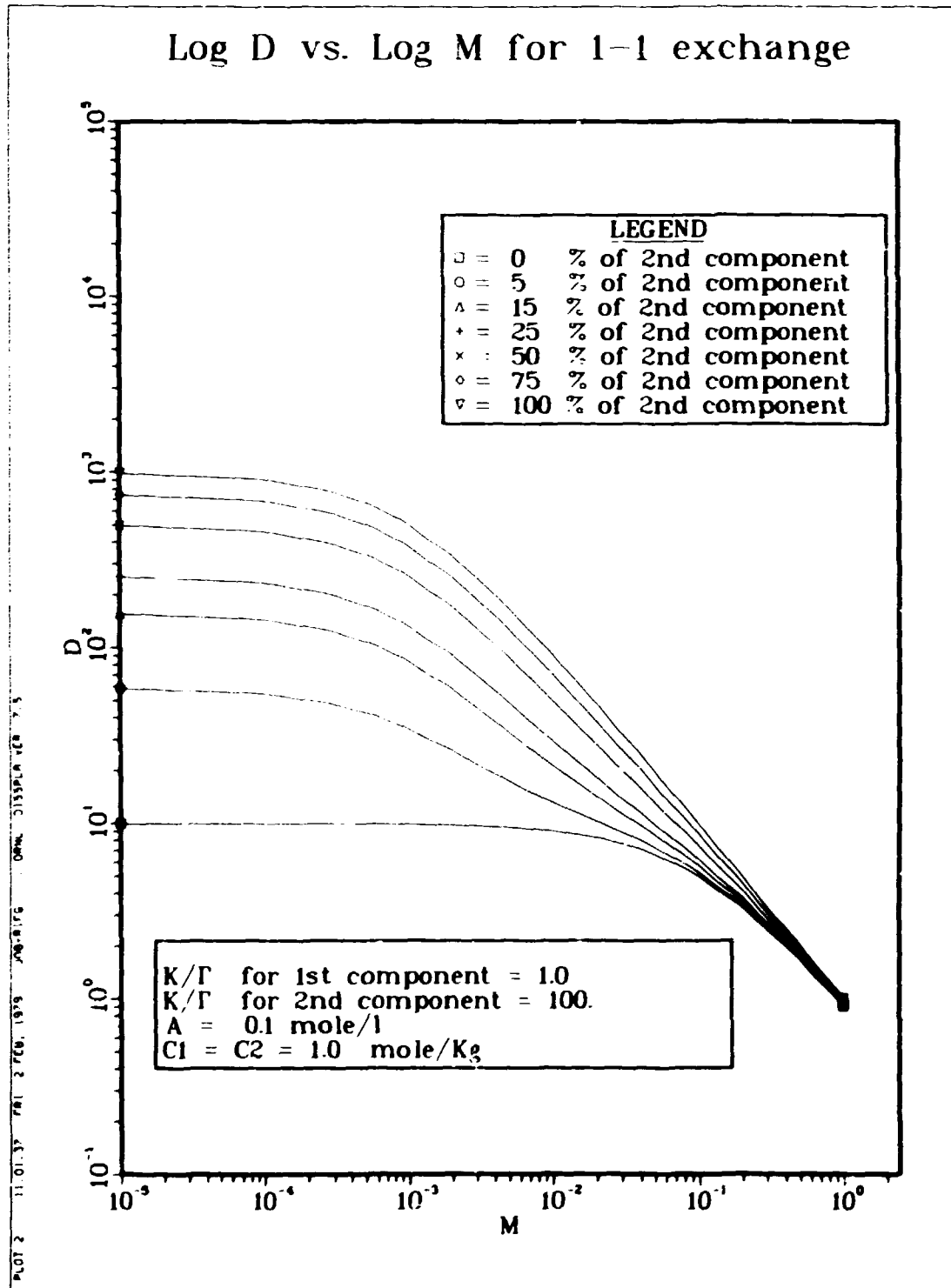


Figure 13

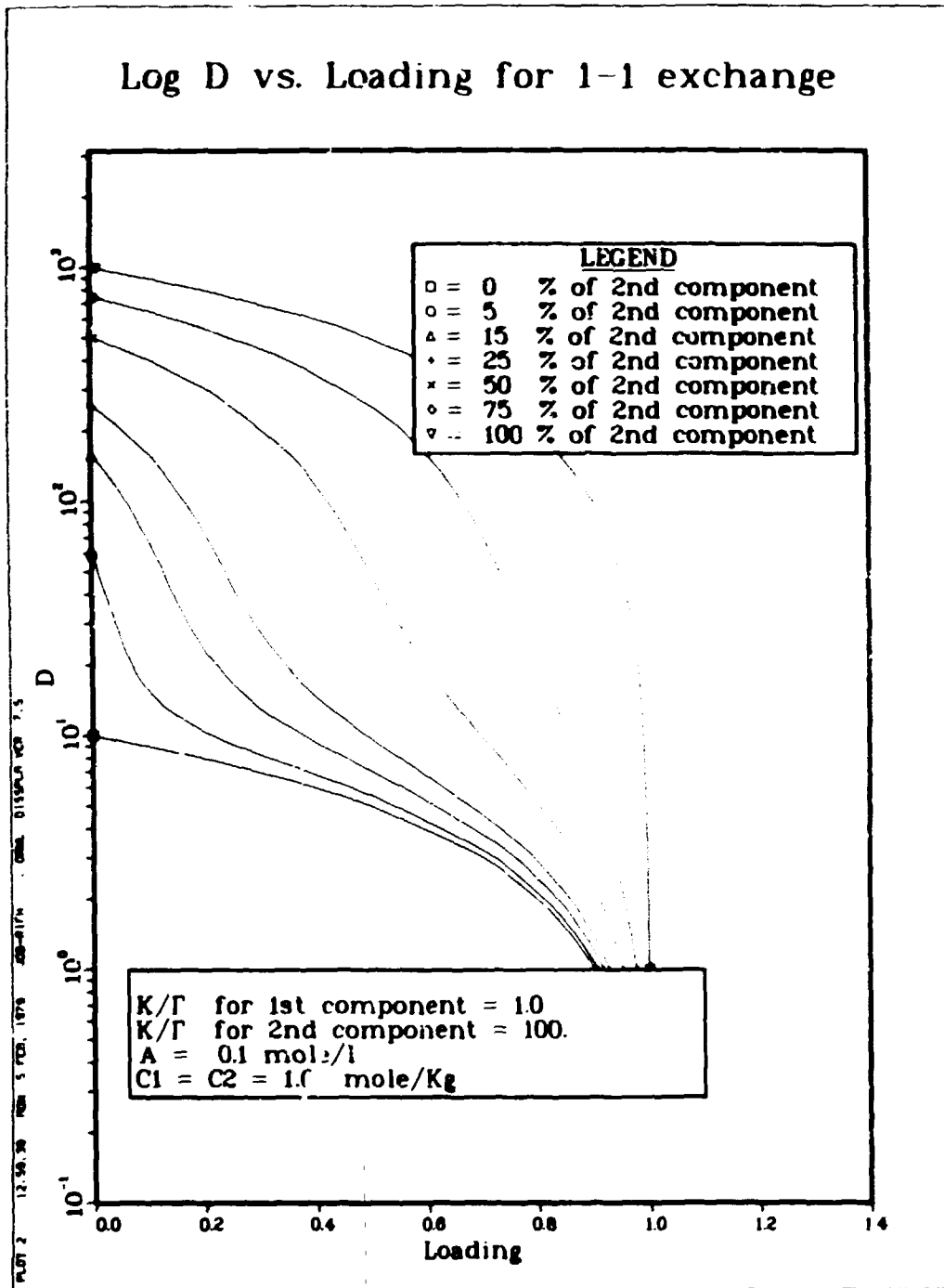


Figure 14

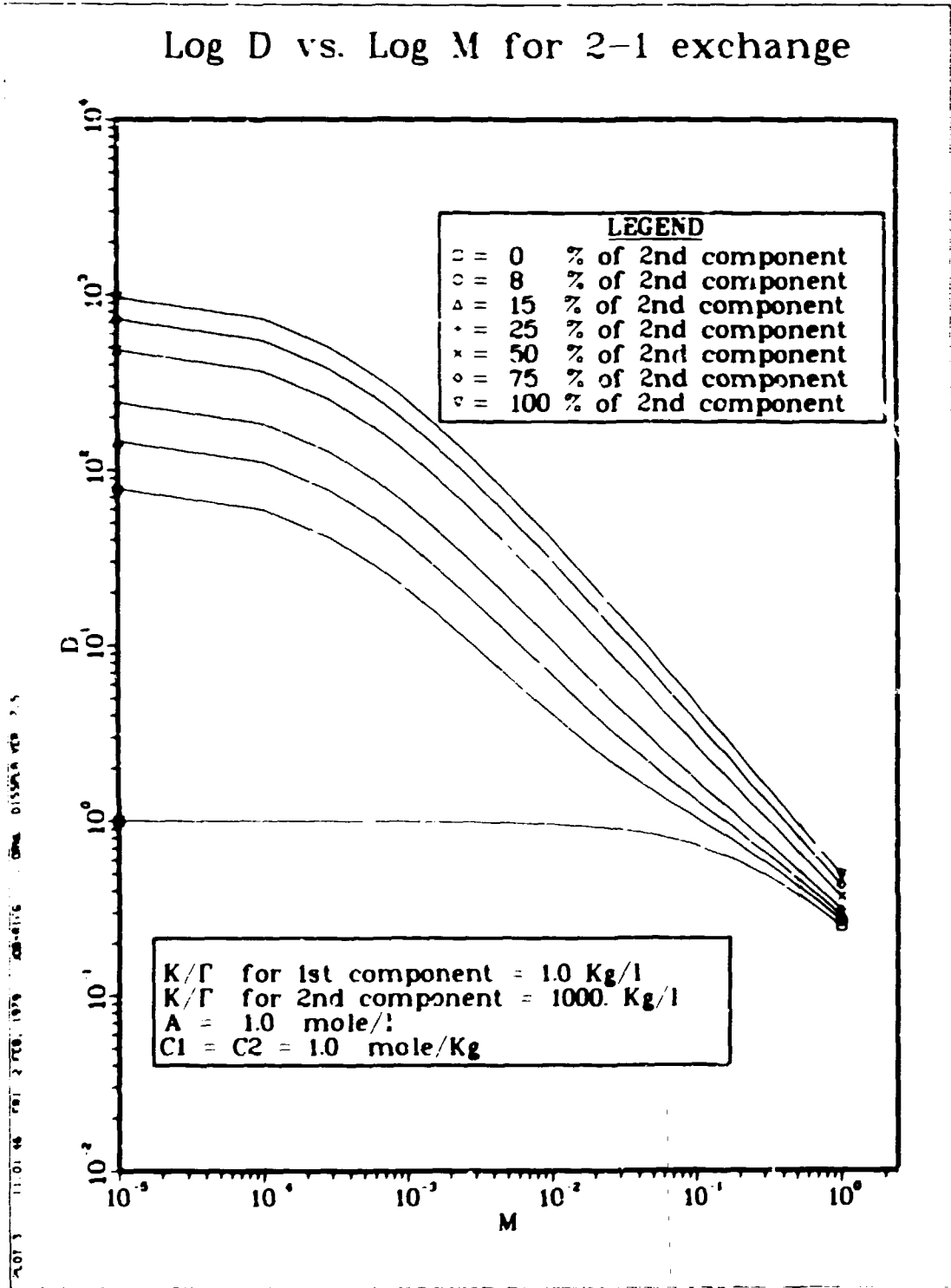


Figure 15

Log D vs. Loading for 2-1 exchange

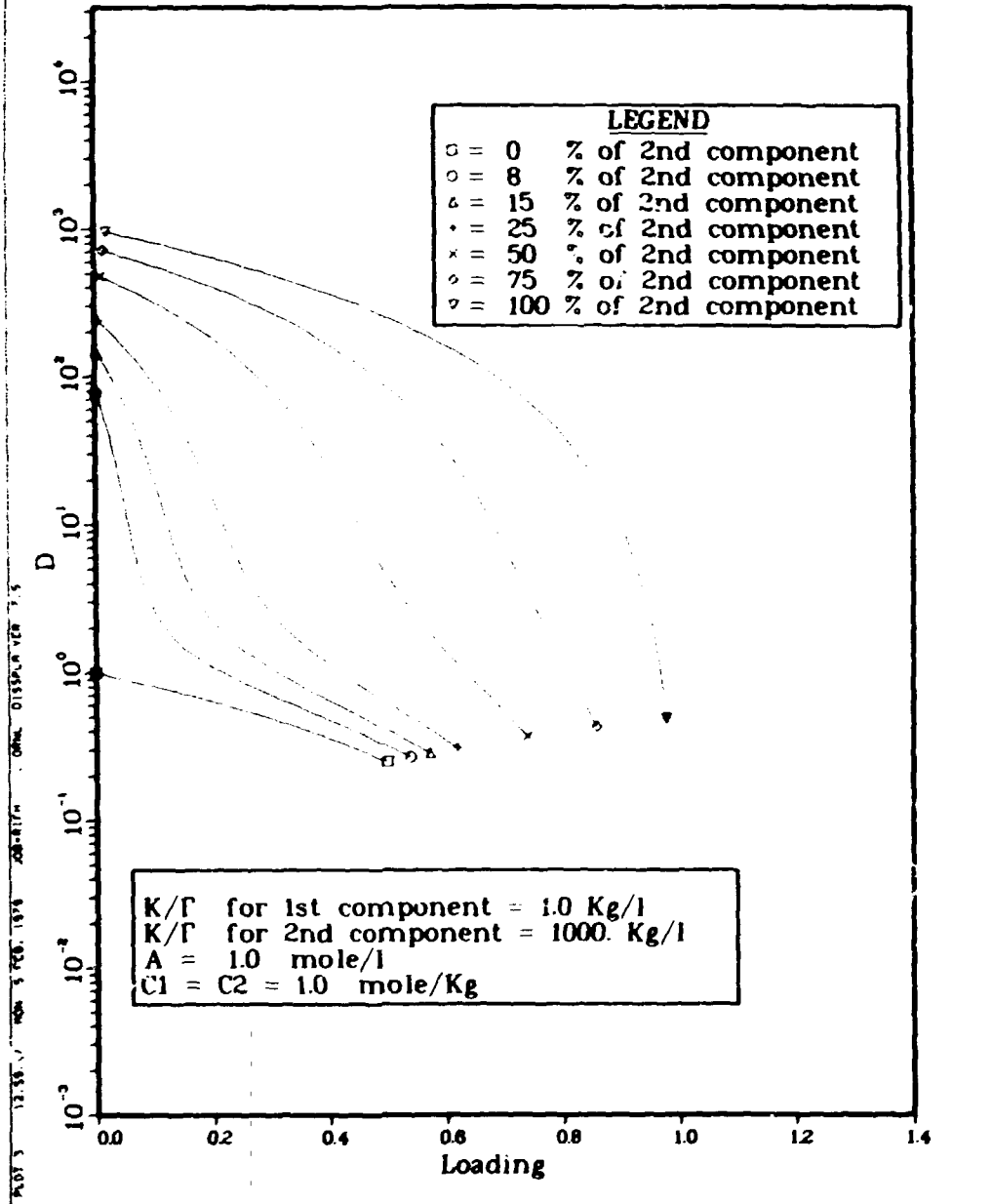


Figure 16

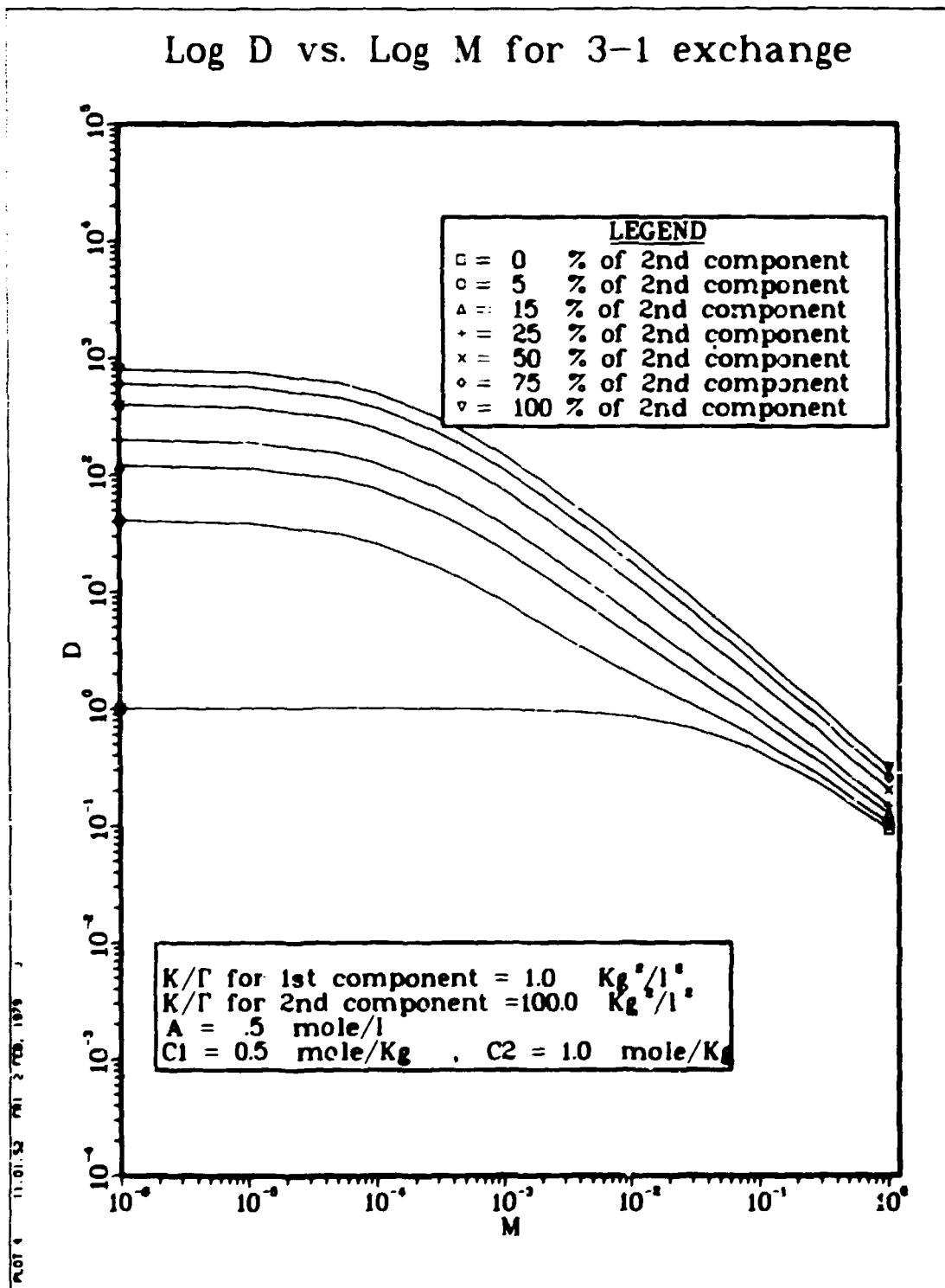


Figure 17

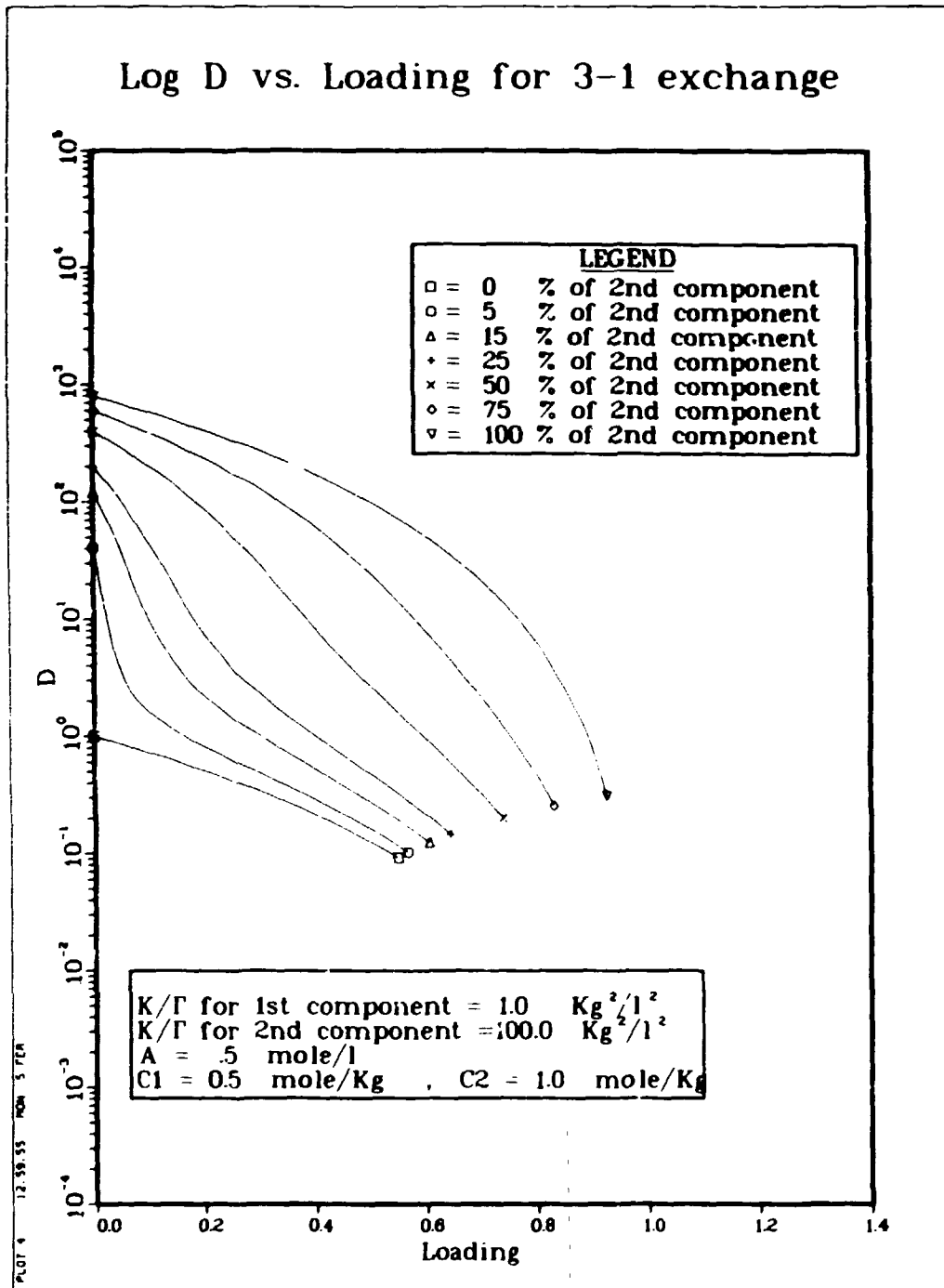


Figure 18

APPENDIX 1

Description of the Mathematics in the Computer Program

The calculations performed by the computer program involve the solution of equation (3) for the value of \bar{m}_M for each adsorber in the mixture with a range of fixed values of the other quantities in the equation. The values of \underline{D} , the distribution coefficient, and \underline{L} , the loading, are computed for each adsorber under specified conditions. These values are then combined to give the overall values of \underline{D} and \underline{L} for the mixed adsorber.

With \underline{n} and \underline{p} both equal to one (1-1 exchange) equation (3) can be solved directly for \bar{m}_M . However, higher order equations must be solved when \underline{n} and/or \underline{p} are greater than unity. Thus different methods would have to be used in the latter cases, not only to solve for the roots of the equations, but also to choose the appropriate root for the computation of \underline{D} and \underline{L} . In order to make the computer program as compact and efficient as possible, the same method is used for all three cases. This results in a slight loss of efficiency for the case where \underline{n} and \underline{p} are equal to one. This is more than offset, however, by the gain in efficiency for the cases where \underline{n} or \underline{p} are greater than unity.

In the computer program equation (3) is solved numerically for the value of \bar{m}_M for each adsorber using the Newton-Raphson method. In implementing this method we rearrange equation (3) and define

$$f(\bar{m}_M) = \frac{K}{r} \frac{m_M^p}{(pm_A^n)} (C - nm_M)^n - \bar{m}_M^p. \quad (25)$$

Suppose $\bar{m}_{M(0)}$ is an initial estimate of the value of the desired root of equation (25). Then an improved estimate of the root is given by

$$\bar{m}_{M(1)} = \bar{m}_{M(0)} + \Delta\bar{m}_M \quad (26)$$

where

$$\Delta\bar{m}_M = \frac{f(\bar{m}_{M(0)})}{f'(\bar{m}_{M(0)})} \quad (27)$$

In this equation $f'(\bar{m}_{M(0)})$ represents the derivative of $f(\bar{m}_M)$ with respect to \bar{m}_M evaluated for the initial estimate of the root $\bar{m}_{M(0)}$. The derivative of equation (25) with respect to \bar{m}_M is given by

$$f'(\bar{m}_M) = -\frac{K}{\Gamma} \frac{(\bar{m}_M)^p}{(\rho\bar{m}_A)^n} (n^2) (C - n\bar{m}_M)^{n-1} - p\bar{m}_M^{p-1} \quad (28)$$

The value of $\bar{m}_{M(1)}$ is then used similarly to obtain a better estimate of the value of the root, and the process is continued until the difference between successive calculated values of \bar{m}_M becomes arbitrarily small.

It can be shown by hand calculation that in the cases with n or $p > 1$ the desired root is the smallest positive root. Hence an initial estimate of \bar{m}_M is taken as 10^{-10} . Convergence upward to the smallest positive root \bar{m}_M is very rapid.

APPENDIX 2

Description of the Computer Program

The computer program, written in Fortran, allows the calculation of the total distribution coefficient and total loading for the adsorption of an ion in solution onto an exchanger containing up to ten adsorbers, each with its own value of K/T and capacity. (Of course all dimensions in the program may be changed to suit the needs of the individual user.) The definitions of the variables which comprise the input and output of the program are shown in Table 1, while Table 2 gives the field and format information for transferring the variables to the input cards.

The program, as listed below, contains a statement CALL DPLLOT. We have not included a plotting routine since such routines are often written to take advantage of the peculiarities of a specific computing system. If the user wishes to plot his output, as we have done in this report, he may supply his own plot package. Since all necessary output variables are stored in subscripted arrays, adapting any plotting routine to the program should be fairly simple.

In order that a prospective user may check out the program at his own installation we have included a sample problem. Values of the input variables for this problem are shown in Table 3. The problem illustrates 2-1 exchange on an adsorber consisting of three exchangers. Output from the program corresponding to the input variables in Table 3 is shown in Table 4. Input cards generating this output are included as the last eight COMMENT cards at the head of the program. In order to use these last

COMMENT cards as input for the sample problem it is only necessary to remove the C from Column 1 and the asterisk from Column 79 on each card.

TABLE 1
DEFINITIONS OF THE VARIABLES WHICH COMPRISE
THE I/O OF THE MAIN PROGRAM*

INPUT

NKGC	Number of different adsorbers in the exchanger (≤ 10), or Number of different values of KG (defined below), or Number of different values of C (defined below).
NA	Number of different values of A (defined below).
NM	Number of different values of M (defined below).
NIT	Maximum number of iterations allowed for convergence.
EN	Valence of the exchangeable ion.
P	Valence of the adsorbed ion.
EPS	Convergence parameter.
C	Exchange capacity of different adsorbers in the exchanger (moles/kg).
KG	K/Γ for different adsorbers in the exchanger.
A	Concentration of supporting electrolyte (moles/l).
M	Equilibrium concentration of exchanged ion (moles/l).
FR	Weight fraction of each adsorber in the exchanger.

OUTPUT

DTOT	Distribution Coefficient
LTOT	Loading fraction of the exchanger

*No description of plotting subroutines is given in the following.

TABLE 2

INPUT DATA FORMAT FOR MAIN PROGRAM

	<u>Field</u>	<u>Variable</u>	<u>Format</u>
Card No. 1	1 - 5	NA	I5
	6 - 10	NM	I5
	11 - 15	NKGC	I5
	16 - 20	NIT	I5
	21 - 30	EN	E10.0
	31 - 40	EPS	E10.0
	41 - 50	P	E10.0
Card No. 2	1 - 10	A ₁	E10.0
	⋮	⋮	⋮
	71 - 80	A ₈	E10.0
Note: If NA > 8 then enough cards to accomodate all values of A will follow.			
Card No. 3	1 - 10	M ₁	E10.0
	⋮	⋮	⋮
	71 - 80	M ₈	E10.0
Note: If NM > 8 enough cards to accomodate all values of M will follow.			
Card No. 4	1 - 10	KG ₁	E10.0
	⋮	⋮	⋮
	71 - 80	KG ₂	E10.0
Note: If NKGC > 8 enough cards to accomodate all values of KC will follow.			
Card No. 5	1 - 10	C ₁	E10.0
	⋮	⋮	⋮
	71 - 80	C ₈	E10.0
Note: If NKGC > 8 enough cards to accomodate all values of C will follow.			
Card No. 6	1 - 10	FR ₁	E10.0
	⋮	⋮	⋮
	71 - 80	FR ₈	E10.0
Note: If NKGC > 8 enough cards to accomodate all values of FR will follow.			

TABLE 3

INPUT VARIABLES FOR THE SAMPLE PROBLEM

<u>Variable</u>	<u>Value</u>	<u>Variable</u>	<u>Value</u>	<u>Variable</u>	<u>Value</u>
NA	5	NM	2	NKGC	3
NIT	100	EN	2.0	EPS	$1.0 \cdot 10^{-7}$
P	1.0	A(1)	0.1	A(2)	0.5
A(3)	1.0	A(4)	2.0	A(5)	4.0
M(1)	$1.0 \cdot 10^{-4}$	M(2)	$1.0 \cdot 10^{-2}$	KG(1)	1.0
KG(2)	$1.0 \cdot 10^3$	KG(3)	$1.0 \cdot 10^5$	C(1)	1.0
C(2)	1.0	C(3)	1.0	FR(1)	0.95
FR(2)	0.04	FR(3)	0.01		

TABLE 4

OUTPUT FROM SAMPLE PROBLEM

2-1 EXCHANGE ON A MIXTURE OF 3 ADSORBERS

THE EXCHANGER CONTAINS 3 COMPONENTS

K/G (1) = 1. C (1) = 1.00E 00 FRACTION = 0.950

K/G (2) = 100E. C (2) = 1.00D 00 FRACTION = 0.040

K/G (3) = 100000. C (3) = 1.00D 00 FRACTION = 0.010

R	A	D	L
1.000D-04	1.000D-01	3.003D 02	6.005D-02
1.000E-04	5.000D-01	1.173D 02	2.347D-02
1.000D-04	1.000D 00	7.013D 01	1.403D-02
1.000E-04	2.000D 00	4.143D 01	8.287D-03
1.000D-04	4.000D 00	2.351D 01	4.702D-03
1.000E-02	1.000D-01	2.620D 01	5.241D-01
1.000D-02	5.000D-01	5.575D 00	1.115D-01
1.000E-02	1.000D 00	3.003D 00	6.005D-02
1.000D-02	2.000D 00	1.997D 00	3.994D-02
1.000E-02	4.000D 00	1.357D 00	2.714D-02

.....

FIXED ADSORBER PROGRAM

INPUT

NKGK IS THE NUMBER OF DIFFERENT ADSORBERS IN THE EXCHANGER (LE. 13), OR
 THE NUMBER OF DIFFERENT VALUES OF KG (DEFINED BELOW), OR
 THE NUMBER OF DIFFERENT VALUES OF C (DEFINED BELOW)
 NA IS THE NUMBER OF DIFFERENT VALUES OF A (DEFINED BELOW)
 NH IS THE NUMBER OF DIFFERENT VALUES OF N (DEFINED BELOW)
 NIT IS THE MAXIMUM NUMBER OF ITERATIONS ALLOWED FOR CONVERGENCE
 EN IS THE VALENCE OF THE EXCHANGEABLE ION (IN ELECTRON UNITS)
 P IS THE VALENCE OF THE ADSORBED ION (IN ELECTRON UNITS)
 EPS IS A CONVERGENCE PARAMETER
 C IS THE EXCHANGE CAPACITY OF DIFFERENT ADSORBERS IN THE EXCHANGER
 EXPRESSED AS MOLE/KG
 KG IS THE RATIO K/GAMMA FOR DIFFERENT ADSORBERS IN THE EXCHANGER
 A IS THE CONCENTRATION OF SUPPORTING ELECTROLYTE IN MOLE/LITRE
 N IS THE EQUILIBRIUM CONCENTRATION OF THE EXCHANGED IONS
 EXPRESSED AS MOLE/LITRE
 PR IS THE WEIGHT FRACTION OF EACH ADSORBER IN THE EXCHANGER

OUTPUT

DTOT IS THE DISTRIBUTION COEFFICIENT
 LTOT IS THE LOADING FRACTION OF THE EXCHANGER

.....

INPUT CARDS FOR THE SAMPLE PROBLEM

5 2 3 100 2. 1. -7 1.
 C0.1 0.5 1.0 2.0 4.0
 1.0000E-4 1.0000E-2

```

C1.0      1.0000E+3 1.0000E+5
C1.0      1.0      1.0
C=0.95    0.04     0.01
C         2-1 EXCHANGE ON A MIXTURE OF 3 ADSORBERS
C 0
IMPLICIT REAL*8 (A-N,O-Z)
REAL*8 N,KG,LOAD,LTOT
DIMENSION A(30),N(30),KG(10),C(10),PR(10),CH(10),PS(10),DPH(10),
1 AN(10),CONV(10),LOAD(10),D(10),DTOT(30,30),LTOT(30,30),TITLE(20)
100 READ (5,1) NA,NN,NRGC,HIT,ZN,EPS,P
1 FORMAT (4I5,3E10.0)
IF(NA .EQ. 0) CALL EXIT
READ (5,2) (A(I),I=1,NA)
READ (5,2) (N(I),I=1,NN)
READ (5,2) (KG(I),I=1,NRGC)
READ (5,2) (C(I),I=1,NRGC)
200 READ (5,2) (PR(I),I=1,NRGC)
2 FORMAT (8E10.0)
IF (PR(1) .EQ. 0.) GO TO 100
DO 500 LA=1,NA
AA=A(LA)
DO 500 NB=1,NN
ZN=N(NB)
DO 210 I=1,NRGC
210 CH(I)=1.0D-10
DO 450 NB=1,HIT
DO 400 I=1,NRGC
PR(I)=KG(I)*ZN/AA*ZN*(C(I)-ZN*CH(I))*ZN-CH(I)**P
ZN1=ZN-1.0D0
PR1=P-1.0D0
DPH(I)=-KG(I)*ZN/AA*ZN*ZN**2*(C(I)-ZN*CH(I))*ZN1-P*CH(I)**PR1
AN(I)=-PR(I)/DPH(I)
400 AN(I)=AN(I)+CH(I)
DO 410 I=1,NRGC
CONV(I)=DABS(AN(I)/CH(I)-1.0D0)
IF(CONV(I)-EPS) 410,410,420
410 CONTINUE
GO TO 460
420 DO 430 I=1,NRGC
430 CH(I)=AN(I)
450 CONTINUE
WRITE(6,10)
10 FORMAT (1H116HDID NOT CONVERGE)
460 DO 470 I=1,NRGC
470 CH(I)=AN(I)
RP=1.0/P
ZNP=ZN/P
DO 480 I=1,NRGC
LOAD(I)=ZN*CH(I)/C(I)
480 D(I)=KG(I)**RP*(C(I)-ZN*CH(I))/AA**ZNP
DT=0.0D0
TL=0.0D0
DO 490 I=1,NRGC
DT=DT+D(I)*PR(I)
490 TL=TL+LOAD(I)*PR(I)

```

```

DTOT(HH,LA)=DT
LYOT(HH,LA)=TL
500 CONTINUE
READ(5,60) (TITLE(KTIT),KTIT=1,20)
60 FORMAT(20A4)
WRITE(6,70) (TITLE(KTIT),KTIT=1,20)
70 FORMAT(1H1,20A4)
WRITE(6,20) NKGCC
20 FORMAT(1H0,' ' THE EXCHANGER CONTAINS',I3,1X,'COMPONENTS'//)
DO 600 I=1,NKGCC
600 WRITE(6,30) I,KG(I),I,C(I),PR(I)
30 FORMAT(1H0,10X,'K/G(',I2,') =',F7.3,5X,'C(',I2,') =',1PE9.2,5X,
1'PFRACTION =',0PF6.3,//)
WRITE(6,40)
40 FORMAT(1H0,10X,'N',10X,'A',12X,'D',10X,'L')
DO 650 NN=1,NN
DO 650 LA=1,NA
650 WRITE(6,50) N(NN),A(LA),DTOT(HH,LA),LYOT(HH,LA)
50 FORMAT(1H0,1PE15.3,E11.3,E11.3,E11.3)
1000 CONTINUE
CALL DPLOT
GO TO 200
END
SUBROUTINE DPLOT
RETURN
END
/*
//GO.FT05P001 DD *
5 2 3 100 2. 1. -7 1.
0.1 0.5 1.0 2.0 4.0
1.0 -4 1.0 -2
1.0 1.0 +3 1.0 +5
1.0 1.0 1.0
0.95 0.04 0.01
2-1 EXCHANGE ON A MIXTURE OF 3 ADSORBERS
/*
//

```


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