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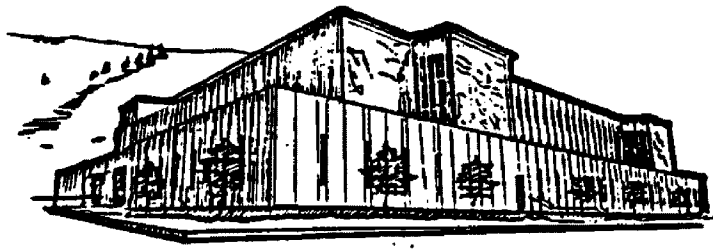
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University of  
**Montana**



A Study of the Adsorption of Binary Solutions onto Solid  
Heterogeneous Surfaces

by

Dan J. Mitchell

B.A., University of Montana--Missoula, 1988

Presented in partial fulfillment of the requirements

for the degree of

Master of Science Chemistry

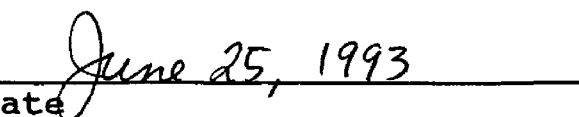
University of Montana

1993

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Mitchell, Dan John, M.S., May 1993 Chemistry

A Study of the Adsorption of Binary Solutions onto Heterogeneous Solid Surfaces

Director: George W. Woodbury, Jr G.W.,

A totally self-consistent thermodynamic model for adsorption onto homogeneous surfaces, which can be generalized to adsorption onto heterogeneous surfaces, was developed. The model was used to interpret a monolayer of adsorption onto the clays, montmorillonite and illite, of binary solutions containing methanol and benzene. The adsorbents had two distinct adsorption regions, polar and non-polar. In our model the non-ideality of the bulk liquid was exactly accounted for with the use of previously evaluated Wilson parameters. The surface phase was assumed ideal. The swelling/disaggregation of the adsorbent was accounted for in the model. Surface parameters of the theory were obtained from isotherm and heats of immersion measurements, measured by Dekany et al.

Our theoretical results were compared to those of Dekany's. Our calculations of the adsorption isotherms were fundamentally different than those of Dekany's, but evident from both Dekany's and our isotherm calculations is the picture of methanol preferentially adsorbing onto the polar surface, and benzene preferentially adsorbing onto the non-polar surface. Our analysis of the heats of immersion differed from those of Dekany's primarily in the correction terms. In Dekany's analysis of the heats of immersion, the bulk liquid mixing terms were omitted. Dekany arbitrarily assigns virtually all the corrections to surface non-ideality. Including surface, bulk liquid, and swelling/disaggregation corrections in our model, we found satisfactory agreement with experiment.

For  
George W. Woodbury Jr  
in gratitude, and respect .

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This thesis deals with the adsorption of binary (non-ionic) liquids onto solid surfaces. The task is to interpret experimental isotherms and heats of adsorption by means of a thermodynamic theory. In doing so, one hopes to gain increased understanding about the nature of solid \ liquid interactions and the adsorption process. From a practical point of view, advances in the theory of adsorption increase our ability to model chemical separation processes that depend on adsorption.

The number of experimental studies of this type on well-characterized surfaces is small. Table I.1 lists those found in the literature, noting only a few having heat measurements.

Table I.1

Liquid Components	Solid Surface(s)	Isotherm	Heats	Ref
benzene cyclohexane	Sheron 6 graphite	yes	no	1
methyl chloroform tert-butylchloride	charcoal	yes	no	1
methyl chloroform carbon tetrachloride	charcoal	yes	no	1
chloroform tetrachloride	charcoal	yes	no	1

n-butylamine benzene	charcoal	yes	no	1
methyl acetate benzene	charcoal	yes	no	1
methyl acetate benzene	charcoal	yes	no	1
methanol benzene	carbon black	yes	no	2
benzene cyclohexane	silica gel	yes	no	3
benzene cyclohexane	coconut- shell charcoal	yes	yes	4
benzene methanol	Carbo Medicinalis No. 5	yes	no	5
dichloroethylene benzene	boehmite	yes	no	6
piridine ethanol	charcoal	yes	no	7
n-heptane cyclohexane	tin-oxide gel	yes	no	8

ethanol benzene	bi-oxides mo-oxides	yes	no	9
benzene nitrobenzene	silica gel alumina	yes	no	10
benzene n-heptane	silica gel	yes	no	10
benzene carbon-tetrachloride	aerosil	yes	no	11
acetic acid benzene	charcoal	yes	no	12
ethylene dichloride benzene	charcoal	yes	no	13
benzene n-heptane	silica gel	yes	no	13
benzene n-heptane	silica gel	yes	no	14
ethanol benzene	titania	yes	no	15

methanol	illite	yes	yes	16
benzene	kaolinite			17
	mont-			18
	morillonite			19
				20
				21

The goal of this thesis is to develop a self-consistent thermodynamic model for adsorption onto heterogeneous surfaces. I. Dekany et al, [16]thru[21], have studied the adsorption of methanol and benzene onto clays: illites, kaolinites, and montmorillonites. The adsorbents have two distinct adsorption regions, polar and non-polar. Na-illite and Na-montmorillonite are naturally polar; non-polar patches are obtained by substituting hexadecyl-pyridium (HDP<sup>+</sup>) cations (long non-polar alkyl chains) for Na<sup>+</sup>. In this way Dekany et al have created well-characterized heterogeneous surfaces which are well tailored for studying the effects of surface heterogeneity on adsorption properties.

The clays of interest are of two types, swelling and non-swelling. Montmorillonite swells and disaggregates when immersed into organic liquids, where illites and kaolinites do not swell [17][19][21]. Montmorillonite is a laminar silicate mineral composed of negatively charged silicate layers stacked in a parallel arrangement. Sodium cations are bound between the silicate layers balancing the charge. The swelling of

HDP-montmorillonite in organic liquids has been concluded by Weiss [17]. Through X-ray diffraction he found that penetration of liquid molecules into the interlamellar space of montmorillonites caused an increase in the basal plane distance. Dekany et al, [17], calculations show that the adsorption capacities increase with the extent of organophilicity, and thus concludes the presence of disaggregation. By the same calculations, Dekany concludes kaolinite disaggregates to a small extent. In this thesis I model one swelling clay--montmorillonite--and one non-swelling clay--illite.

### Experimental

There are two types of thermodynamic experiments: measurements of adsorption isotherms and measurements of heats of immersion. The measured isotherm describes the composition of the adsorbed liquid relative to bulk liquid. The excess isotherm is defined as

$$\frac{n_K^{a(n)}}{m} = \frac{n}{m} (\Delta x_K^l) \quad (I.1)$$

where  $\Delta x_K^l = x_{K,0}^l - x_K^l$

m is the mass of the adsorbent, n is the total moles of the liquid mixture,  $x_{K,0}^l$  is the liquid fraction of the Kth component before adsorption, and  $x_K^l$  is the liquid mole fraction of the Kth component after adsorption is complete. All quantities on the right hand side are measurable, so  $n_K^{a(n)}$

is an experimental quantity. Dekany checks the purity of the components by refractometry. Dried samples (dried in a vacuum) of adsorbents are immersed into the liquid mixture. After 48 hours the adsorbent is removed by centrifugation. The equilibrium liquid mole fraction of the Kth component  $x_K^l$  is determined with a Zeiss liquid-interferometer. The "isotherm" is a plot of  $n_K^{\sigma(n)}/m$  vs  $x_K^l$ .

The heat of immersion  $\Delta H_{imm}^{\sigma}$  is the heat adsorbed when the adsorbent is immersed in an amount of liquid that is large compared to the amount of adsorbent. Upon immersion heat is usually emitted which results in  $\Delta H_{imm}^{\sigma}$  being negative. The energy changes are associated with the attachment of the liquid components to the surface of the adsorbent, the migration of the preferentially adsorbed component out of solution, and the swelling and/or disaggregation of the adsorbent.

#### Dekany et al's analysis of the isotherms

The analysis is based on the following equilibrium which describes the exchange of components between the surface and the liquid.



From (I.2) Dekany obtains the following equilibrium constant

$$K' = \frac{x_2^s a_1^l}{x_1^s a_2^l} \quad (\text{I.3})$$

where  $x_k^s$  is the surface mole fraction of component K,  $a_k^l$  is the activity of the Kth component in solution, and  $K'$  is the equilibrium constant for the process in (I.2). Evident from equation (I.3) are the assumptions that the surface is treated as being ideal and the liquid components of interest are similar in size. Dekany takes surface inhomogeneity into account through the equilibrium constant. He argues[18] that,

$$K' = \frac{(1-\theta_1)\beta}{\theta_1} \quad (\text{I.4})$$

where  $\theta_1$  is the fraction of the non-polar surface,  $a_1$  and  $a_2$  are the cross-sectional areas per mmole of components 1 and 2, and  $\beta$  is  $a_1/a_2$ . The assumptions made in the development of equation (I.4) are that the polar components stick to the polar regions of the adsorbent and the non-polar components stick to the non-polar regions of the adsorbent. Equations (I.3) and (I.4) imply

$$x_2^s(x_2^l) = \frac{x_2^l}{\frac{\theta_1}{(1-\theta_1)\beta} \left( \frac{\gamma_1^l}{\gamma_2^l} \right)^{x_1^l + x_2^l}} \quad (\text{I.5})$$

where  $\gamma_k^l$  is the activity coefficient of the Kth component in the bulk liquid.



$$\gamma_K^I = \frac{a_K^I}{x_K^I} \quad (I.6)$$

Equation (I.5) is translated to a theoretical expression for the isotherm as follows. The assumption that the adsorbed layer is a monolayer gives (I.7),

$$a_1 \frac{n_1^s}{m} + a_2 \frac{n_2^s}{m} = a_{equ}^s \quad (I.7)$$

where  $a_{equ}^s$  is the equivalent specific area ( $m^2/g$ ),  $n_1^s/m$  and  $n_2^s/m$  are the mmoles of components 1 and 2 in the interfacial region per unit mass of adsorbent. Equations (I.1) and (I.7) imply [16]

$$\frac{n_K^{a(n)}}{m} = \frac{n^s}{m} (x_K^s - x_K^I) \quad (I.8)$$

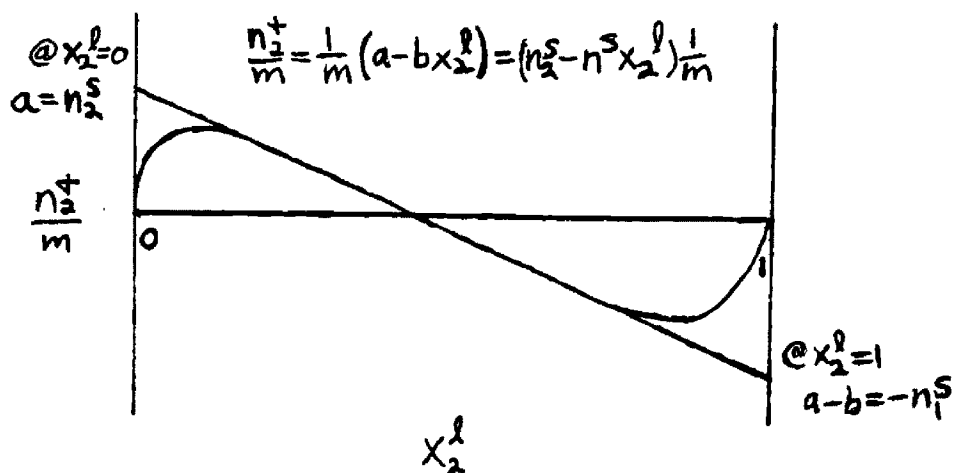
where

$$n^s = n_1^s + n_2^s \quad (I.9)$$

Equations (I.5) and (I.8) gives the isotherm.

Dekany calculates  $n_K^{a(n)}$  from equation (I.8) as follows. The surface mole fraction  $x_K^s$  is determined from equation (I.5),  $\beta=1.8947$ [18] and the activity coefficients originate from liquid vapor equilibrium data[35]. The quantities  $n_1^s/m$  and  $n_2^s/m$  are obtained from the linear portion of the S-shaped isotherm, using Schay's graphical extrapolation method

[16] (see figure below).



The surface fraction  $\theta$ , may be obtained in two distinct ways. For the first we use equation I.10 below, where  $a_{equ}^s$  is obtained from equation I.7, and where  $n_1^s$  and  $n_2^s$  in I.7 come from Schay's construction.

$$\theta_1 = \frac{n_1^s a_1}{m a_{equ}^s} \quad (I.10)$$

$\theta_1$  can also be obtained directly by

$$\theta_1 = \frac{a_{HDP^+}^s}{a_{equ}^s} \quad (I.11)$$

where  $a_{HDP^+}^s = (\text{mmole HDP}) (a_m \text{HDP}^+)$

$a_{HDP^+}^s$  is the area of the  $\text{HDP}^+$  cation per mass of adsorbent, (mmole HDP) is the number of mmoles of the  $\text{HDP}^+$  cation that has been exchanged with the resident cation per mass of adsorbent, and  $a_m \text{HDP}^+$  is the area covered by 1 mmole of  $\text{HDP}$  ( $1728 \text{ m}^2/\text{mmole}$  [18]). Equation (I.10) contains Dekany's

assumptions about the adsorption process (polar components stick to polar patches, non-polar components stick to non-polar patches, monolayer adsorption, and ideal surface) while equation (I.11) only assumes monolayer adsorption. Dekany compares values of  $\theta_1$  from equation (I.10) and (I.11)--see tables I.2 and I.3--to test his assumptions; agreement is

---

Table I.2

	$\theta_1(I.11)$	$\theta_1(eq.I.10)$
Na-mont	0	0
mont-1	0.325	0.321
mont-2	0.534	0.579
mont-3	0.635	0.660
mont-4	0.678	0.711
mont-5	0.774	0.759
mont-6	0.842	0.811

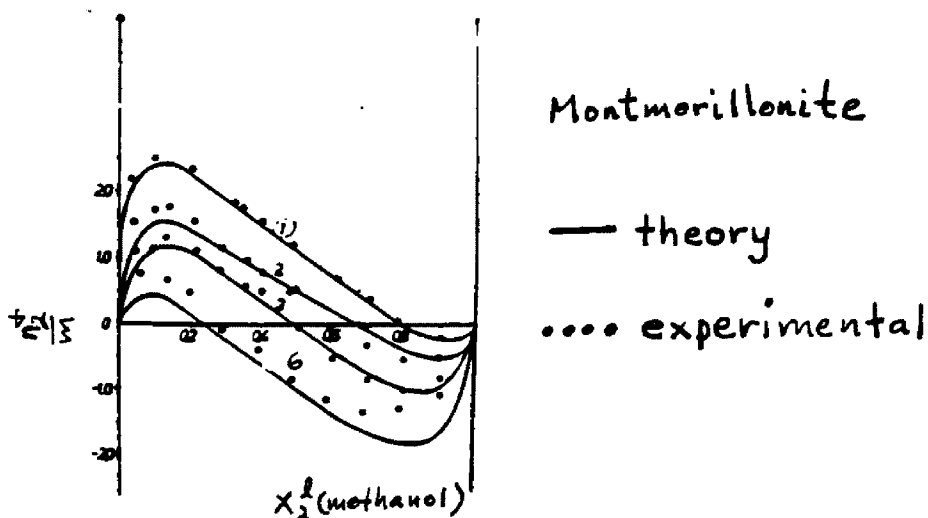
Table I.3

	$\theta_1(I.11)$	$\theta_1(eq.I.10)$
Na-illite	0	0
illite-1	0.404	0.566
illite-2	0.562	0.660
illite-3	0.728	0.737
illite-5	0.986	0.890

---

generally good.

The figure [18] below shows the comparison of the theoretical isotherms from equation (I.5) and (I.8) and the measured montmorillonite isotherms.



The fits are good, but this is not a sensitive test of the theory, for the way  $n_1^s$  and  $n_2^s$  are extracted from the experimental isotherm guarantees that the theoretical isotherm will fit the experimental isotherm in the linear region.

Dekany's theory will not work for a homogeneous surface because of the built-in assumption that the polar component always sticks to the polar adsorbent and the non-polar component sticks to the non-polar adsorbent; the assumption is not tenable if the adsorbent is either all polar or all non-polar. This can be seen from equation (I.4), where in the case of a homogeneous surface  $\theta_1$  must equal 1 or 0.  $K'$  then equals 0 or  $+\infty$ . Dekany's theory attributes the azeotropic point (where  $x_i^s = x_i^l$ ) to the heterogeneity of the surface;

however it is well known that non-ideal solutions on homogeneous surfaces can exhibit azeotropes (see Fig. 22 for an example). The size effects of the liquid components are treated inconsistently. In equation (I.3) they are completely ignored, while in equations (I.7) they are included.

In spite of these criticisms, Dekany has shown that his simple picture of adsorption on a heterogeneous surface is consistent with the measured isotherms. Heats of immersion provide a more sensitive test.

#### Dekany et al analysis of the heat of immersion

Dekany's theoretical formula of  $\Delta H_{imm}^{\infty}$  for a non-swelling adsorbent with a homogeneous surface is

$$\Delta H_{imm}^{\infty} = H_{eq} - H_i \quad (I.12)$$

where  $H_i$  and  $H_{eq}$  are the enthalpies before and after immersion, respectively. The initial enthalpy  $H_i$  is given by

$$H_i = n_1 h_1 + n_2 h_2 + H^e(n_1, n_2) + m h^s \quad (I.13)$$

where  $h_1$  and  $h_2$  are the molar enthalpies of pure components 1 and 2,  $h^s$  is the specific enthalpy of the solid adsorbent,  $n_1$  and  $n_2$  are the moles of component 1 and 2,  $m$  is the mass of the adsorbent, and  $H^e(n_1, n_2)$  is the excess enthalpy function of the bulk liquid. The enthalpy after immersion is

$$H_{eq} = n_1^l h_1 + n_2^l h_2 + H^e(n_1^l, n_2^l) + m h^s + n_1^s h_1^s + n_2^s h_2^s + H^{se}(n_1^s, n_2^s) \quad (I.14)$$

$n_k^l$  is the amount of component  $k$  in the bulk liquid,  $n_k^s$  is the amount of component  $k$  in the adsorption layer,  $h_1^s$  and  $h_2^s$  are the molar enthalpies of components 1 and 2 in the adsorption layer, and  $H^{se}(n_1^s, n_2^s)$  is the excess enthalpy function of the adsorption layer. Dekany ignores the contribution from bulk mixing to give

$$\Delta H_{imm}^w = n_1^s (h_1^s - h_1) + n_2^s (h_2^s - h_2) + H^{se}(n_1^s, n_2^s) \quad (I.15)$$

Rearrangement of equation (I.15) gives

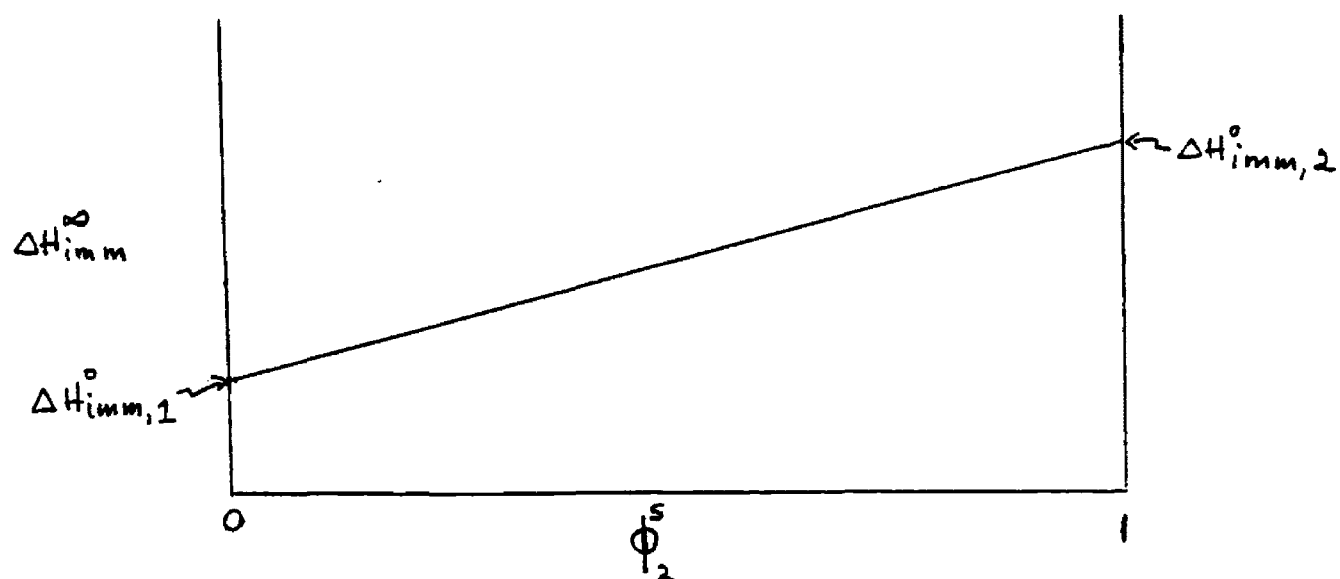
$$\Delta H_{imm}^w = \phi_1^s \Delta H_{imm,1}^o + \phi_2^s \Delta H_{imm,2}^o + H^{se}(n_1^s, n_2^s) \quad (I.16)$$

$$\text{where } \phi_k^s = \frac{n_k^s}{n_k^{s,o}} \quad , \quad \Delta H_{imm,k}^o = n_k^{s,o} (h_k^s - h_k)$$

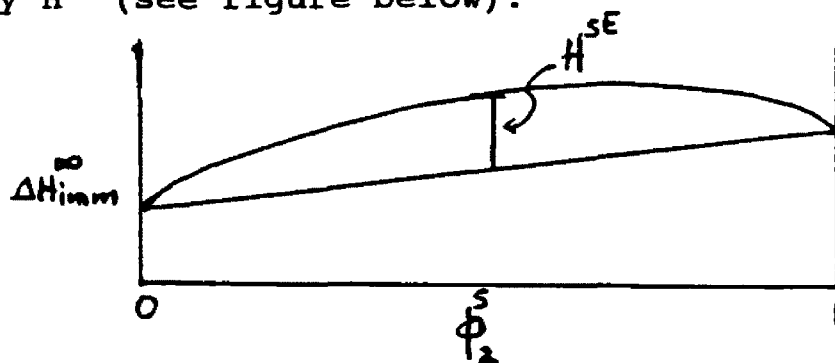
$\phi_k^s$  is the volume fraction of component  $k$  in the adsorption layer where  $n_k^{s,o}$  is the adsorption capacity of pure component  $k$  (i.e. the number of moles of pure component  $k$  required to cover the surface).  $\Delta H_{imm,k}^o$  is the enthalpy of immersion for pure component  $k$ .

For an "ideal" surface we have the definition  $H^{se}=0$ ;

equation (I.16) then becomes linear in  $\phi_2^s$ .

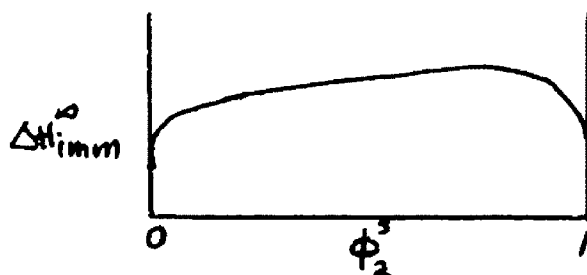


If measured values of  $\Delta H_{imm}^\circ$  are not linear but increase monotonically with  $\phi_2^s$ , Dekany then uses the ideal portion of equation (I.16) for analysis, calling the deviation from ideality  $H^{se}$  (see figure below).

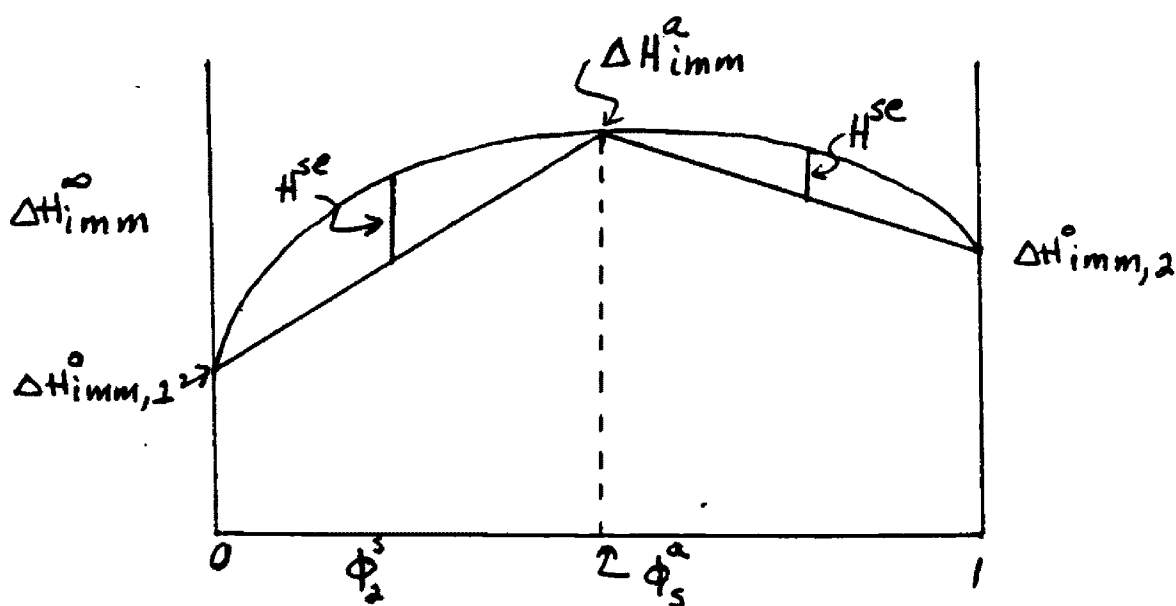


For heterogeneous surfaces the isotherm is usually S-

shaped with heat curves that typically look like



where the maximum value in  $\Delta H_{imm}^{\circ}$  vs  $\phi_2^s$  is near the azeotropic composition  $\phi_2^a$ . In this case Dekany defines the "ideal" heat as shown in the figure below.

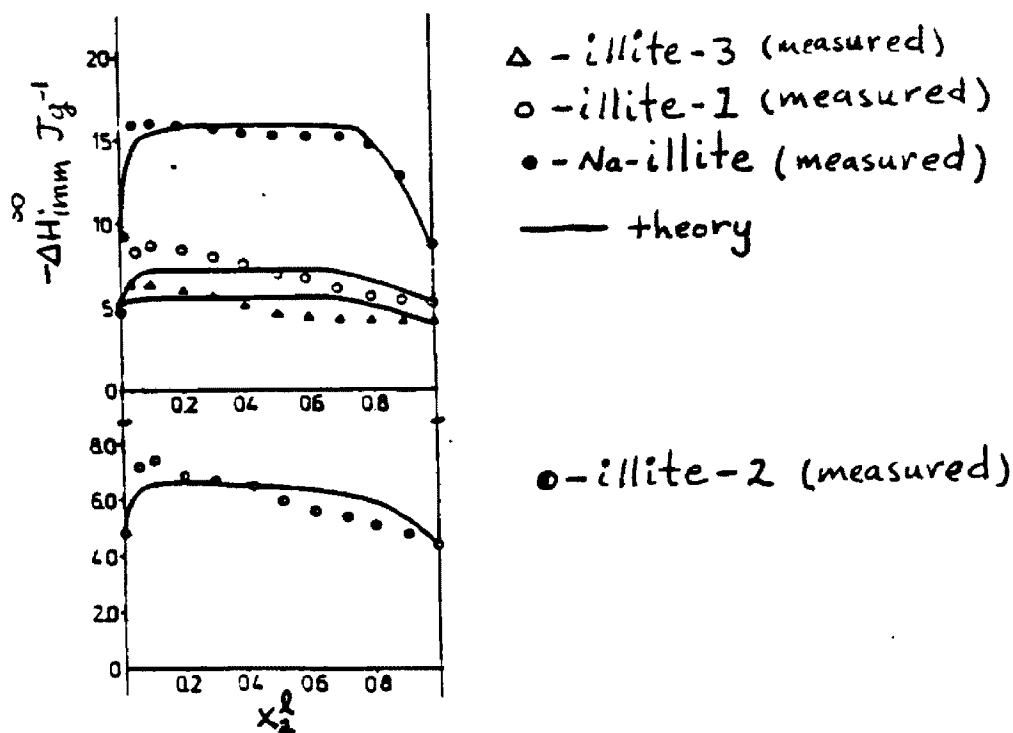


Here  $\Delta H_{imm}^a$  and  $\phi_2^a$  are the heat of immersion and the surface volume fraction at the azeotrope. The difference between the experimental and the ideal heats is  $H^{se}$  according to Dekany et al. We may rationalize this "two-segment ideal model" as follows. Suppose surface A is non-polar, surface B is polar, component 1 is non-polar, and component 2 is polar. Assume that the polar component sticks to the polar adsorbent and the non-polar component sticks to the non-polar adsorbent.

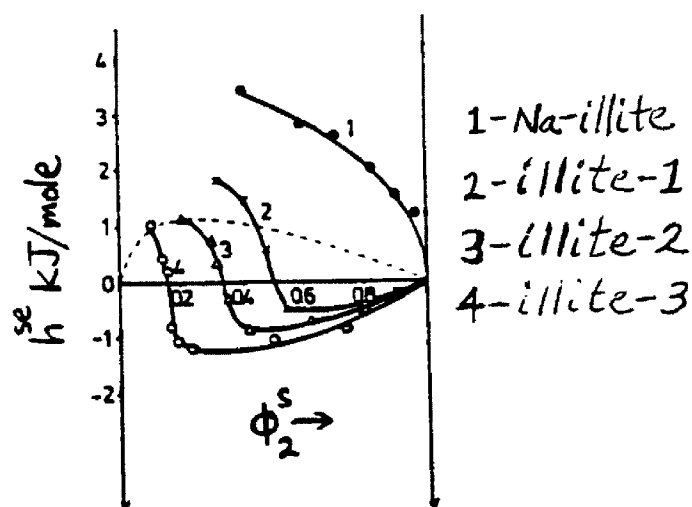


Then in the range of  $\phi_2^s$  from 0 to  $\phi_2^a$ , surface B goes from no adsorption of component 2 to being completely covered by component 2, and surface A is completely covered by component 1 throughout the range. In the range of  $\phi_2^s$  from  $\phi_2^a$  to 1, surface B is completely covered by component 2 throughout the range, and surface A goes from being completely covered by component 1 to no coverage. Thus adsorption onto surface A is observed when  $\phi_2^a < \phi_2^s < 1$ , and adsorption onto surface B is observed when  $0 < \phi_2^s < \phi_2^a$ .

Dekany analyzes all the illites using the two-segment ideal model. The figure below [21] shows how well the two segment, ideal model fits the experimental heat of Na-illite. Dekany concludes that Na-illite is nearly ideal.



The two-segment ideal model is inconsistent in describing  $\Delta H_{imm}^{\circ}$  for Na-illite. One would expect  $\Delta H_{imm}^{\circ}$  vs  $\phi_2^s$  to increase monotonically since the Na-illite surface is homogeneous and the isotherm is U-shaped. Comparisons of the two-segment ideal model with experimental HDP-illite heats (see page 16) [21] cause Dekany to conclude that adsorption is not ideal on these surfaces.



The non-ideal contributions are shown in the figure above [21] where  $h^{se}$  is the molar excess surface enthalpy:  $h^{se} = H^{se}/n^s$ . From the figure one sees in general that the heats from the molar excess enthalpies of the adsorption layer and the bulk liquid (dashed line) are not similar. One would expect the interactions to be similar in both cases, and thus producing similar heat effects. With this in mind one questions Dekany's choice of ignoring the bulk liquid mixing terms.

Analysis of the swelling adsorbents is similar to the analysis of non-swelling adsorbents. For homogeneous surfaces equation (I.16) is modified as follows

$$\Delta H_{imm}^{\infty} = \phi_1^s \Delta H_{imm,1}^{o,c} + \phi_2^s \Delta H_{imm,2}^{o,c} + H^{se}(n_1^s, n_2^s) + \Delta_{sw}H \quad (I.17)$$

where  $\Delta H_{imm,1}^{o,c} = [n_1^{s,o} + \Delta n_1^{s,o}](h_1^s - h_1) + [n_2^{s,o} + \Delta n_2^{s,o}](h_2^s - h_2)$

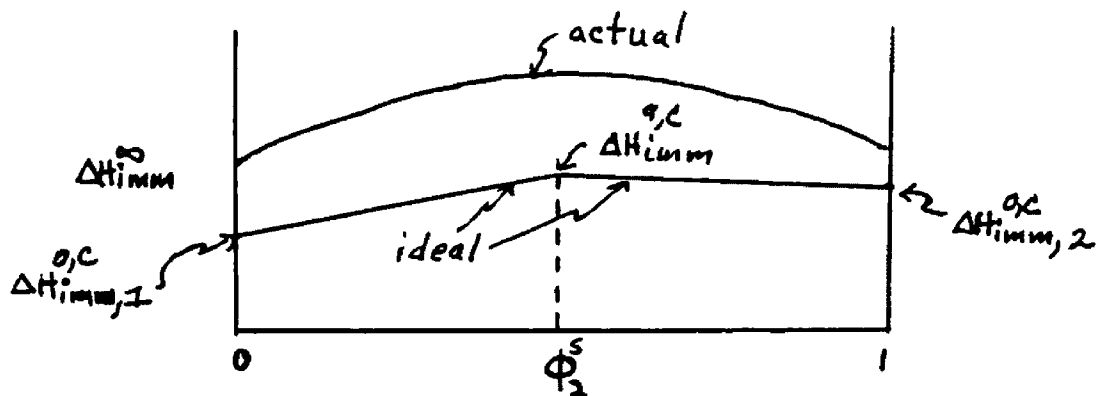
where  $\Delta n_k^{s,o}$  is the change in the adsorption capacity of component k due to swelling. The effect of swelling is contained partly in the term  $\Delta_{sw}H$ , and partly in the terms  $\Delta H_{imm,1}^{oc}$  and  $\Delta H_{imm,2}^{oc}$ .  $\Delta H_{imm,k}^{o,c}$  is a formal quantity related to the measured heat of immersion in pure component k,  $\Delta H_{imm}^o$  by

$$\Delta H_{imm,k}^o = \Delta H_{imm,k}^{o,c} + \Delta_{sw}H(\text{pure } k) \quad (I.18)$$

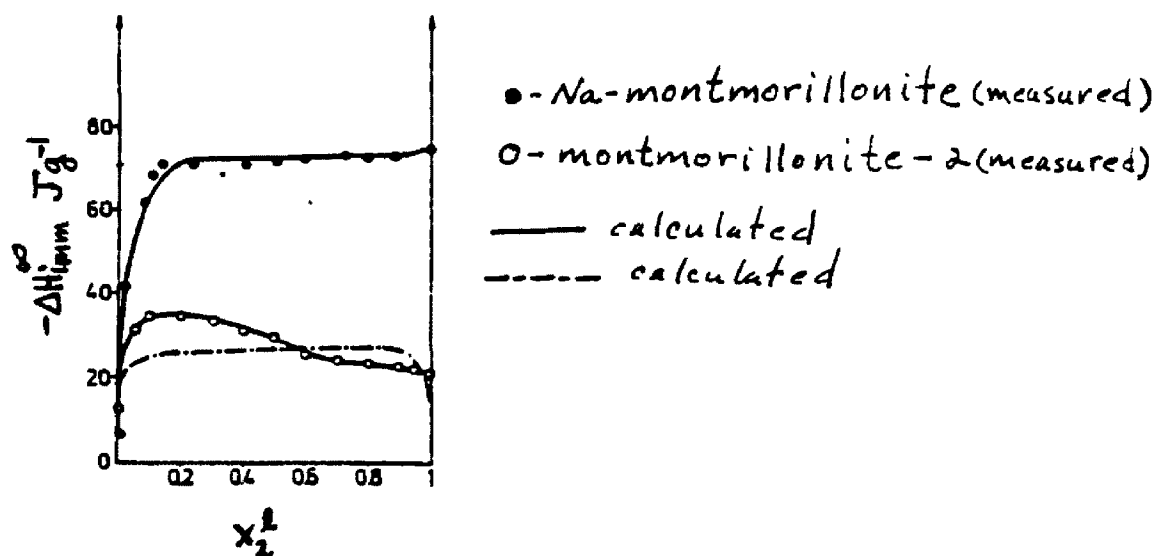
For ideal adsorption onto a homogeneous surface the terms  $\Delta H_{imm,1}^{o,c}$  and  $\Delta H_{imm,2}^{o,c}$  make up the ideal portion of the heat of immersion, and thus equation (I.17) becomes

$$\Delta H_{imm}^{\infty} = \Delta H_{imm,ideal}^{\infty} + H^{se}(n_1^s, n_2^s) + \Delta_{sw}H \quad (I.19)$$

For ideal adsorption onto a heterogeneous surface, Dekany uses equation (I.19), but  $\Delta H_{imm,ideal}^{\infty}$  is defined in terms of the two-segment ideal model(model used for the illites). The fixed points used are  $\Delta H_{imm,1}^{o,c}$ ,  $\Delta H_{imm,2}^{o,c}$ , and  $\Delta H_{imm}^{a,c}$ .  $\Delta H_{imm}^{a,c}$  is the hypothetical heat of immersion at the azeotropic composition if no swelling is present(see figure on next page).



Dekany analyzes the heat of immersion for Na-montmorillonite by using the ideal portion of equation (I.17). From the figure below, Dekany concludes that Na-montmorillonite is nearly ideal. For HDP-montmorillonite, Dekany uses the two-segment, ideal model for heat of immersion calculations. From the figure below [21], a large deviation from ideality is seen.



This deviation Dekany et al attribute to swelling and surface mixing in accordance with equation I.19, which is rearranged to

$$H^{se} + \Delta H_{sw} = \Delta H_{imm}^{\infty} - \Delta H_{imm,ideal}^{\infty} \quad (I.20)$$

Arguing that  $H^{se}$  is similar in magnitude to the illites, and hence small, Dekany concludes most of the deviation is due to swelling. Dekany et al's calculations of  $H^{se}$  and  $\Delta H_{sw}$  are suspect. It was seen that the excess enthalpies of the adsorption layer and the bulk liquid are quite different, thus values calculated for  $H^{se}$  may not be representative of the heat effects in the adsorption layer. Secondly,  $H^{se}$  depends on the choice of ideal models, and the ideal model for heterogeneous surfaces is totally ad hoc. Dekany is inconsistent in treating homogeneous surfaces. For Na-illite, the ideal model for a heterogeneous adsorbent is used, and for Na-montmorillonite the ideal model for a homogeneous surface is used. Dekany ignores bulk mixing terms, hiding their heat effects in the  $H^{se}$  term. Since  $\Delta H_{sw}$  depends on the evaluation of  $H^{se}$ , it also is suspect for the reasons mentioned above.

Another weakness of Dekany's model is that it can not be generalized to other types of systems; it is specific for surfaces with two types of patches.

It is our goal to develop a totally self-consistent thermodynamic model for adsorption onto homogeneous surfaces, which can be generalized to adsorption onto heterogeneous surfaces. In this model, bulk liquid mixing terms will be

exactly accounted for. Using this model we will see if our conclusions are significantly different from those of Dekany et al's for these systems.

## II. Theory

### Fundamental surface equations

The system of interest consists of a binary solution with  $n_1$  and  $n_2$  moles of components one and two. In the solution is suspended an adsorbent of mass  $m$ . The fundamental equation for the system [29] is

$$dE = TdS - PdV + \mu_1 dn_1 + \mu_2 dn_2 + u dm \quad (\text{II.1})$$

where  $u$  is the chemical potential per unit mass of the adsorbent(solid) and  $V$  is the total volume of the system (solid and liquid). By use of standard thermodynamic definitions

$$A = E - TS \quad (11.2)$$

$$G = A + PV \quad (11.3)$$

and application of the Legendre transformations, equation (II.1) is transformed to

$$dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 + udm \quad (\text{II.4})$$

The reference systems [29] used to define surface properties have the following fundamental equations.

$$dA^c = -S^c dT + u^c dm \quad (\text{II.5})$$

$$dG^l = -S^l dT + V^l dP + \mu_1 dn_1^l + \mu_2 dn_2^l \quad (\text{II.6})$$

Equation (II.5) defines the Helmholtz free energy of pure adsorbent of mass  $m$  in a vacuum. Equation (II.6) is the Gibbs free energy of the bulk liquid, where the bulk liquid has the same intensive properties ( $T, P, \mu_1, \mu_2$ ) as the liquid far from the surface in the surface system [29].



Surface excess properties are defined [29] by

$$\begin{aligned}
 G^s &= G(T, P, n_1, n_2, m) - G^1(T, P, n_1^1, n_2^1) - A^c(T, m) \\
 S^s &= S(T, P, n_1, n_2, m) - S^1(T, P, n_1^1, n_2^1) - S^c(T, m) \\
 H^s &= H(T, P, n_1, n_2, m) - H^1(T, P, n_1^1, n_2^1) - E^c(T, m) \\
 V^s &= V(T, P, n_1, n_2, m) - V^1(T, P, n_1^1, n_2^1) \\
 u^s &= u(T, P, n_1, n_2, m) - u^c(T, m) \\
 n_i^s &= n_i - n_i^1
 \end{aligned} \tag{II.7}$$

From equations (II.4) thru (II.7) equations for the surface properties are derived [29]

$$dG^s = -S^s dT + V^s dP + \mu_1 dn_1^s + \mu_2 dn_2^s + u^s dm \tag{II.8}$$

Eulers theorem on homogeneous functions states that the Gibbs free energy is related to the chemical potential through the equation

$$G^s = \mu_1 n_1^s + \mu_2 n_2^s + u^s m \tag{II.9}$$

By changing the independent variables from  $T, P, n_1^s, n_2^s$  to  $T, P, \mu_1, \mu_2$  and carrying out the Legendre transformation on equation (II.8) we obtain the surface Gibbs-Duhem equation

$$0 = -S^s dT + V^s dP - n_1^s d\mu_1 - n_2^s d\mu_2 - m du^s \quad (\text{II.10})$$

### Immersion Properties

The changes in thermodynamic properties that accompany the immersion of adsorbent in solution at fixed T and P are called immersion properties. Some are defined below [29]

$$\begin{aligned} \Delta G_{imm} &= G(T, P, n_1, n_2, m) - G^l(T, P, n_1, n_2) - A^c(T, m) \\ \Delta S_{imm} &= S(T, P, n_1, n_2, m) - S^l(T, P, n_1, n_2) - S^c(T, m) \\ \Delta V_{imm} &= V(T, P, n_1, n_2, m) - V^l(T, P, n_1, n_2) \\ \Delta H_{imm} &= H(T, P, n_1, n_2, m) - H^l(T, P, n_1, n_2) - E^c(T, m) \end{aligned} \quad (\text{II.11})$$

Immersion properties are important because they are measurable.

We relate immersion properties to the surface properties as follows. Equations (II.11) and (II.7) imply

$$\Delta G_{imm} = G^s - G^l(T, P, n_1, n_2) + G^l(T, P, n_1^l, n_2^l) \quad (\text{II.12})$$

$$G^l(T, P, n_1, n_2) = G^l(T, P, n_1^l + n_1^s, n_2^l + n_2^s) \quad (\text{II.13})$$

If the solid is immersed in a large amount of liquid

equation (II.13) can be expanded in  $n_1^s/n_1^l$  and  $n_2^s/n_2^l$  by using the familiar Taylor's series for a function of two variables. We use

$$G^l(T, P, n_1^l + n_1^s, n_2^l + n_2^s) = G^l\left(T, P, n_1^l \left(1 + \frac{n_1^s}{n_1^l}\right), n_2^l \left(1 + \frac{n_2^s}{n_2^l}\right)\right)$$

where

$$\frac{n_1^s}{n_1^l} = \delta_1$$

$$\frac{n_2^s}{n_2^l} = \delta_2$$

Expansion of (II.13) and truncation of the non-linear terms give

$$G^l(T, P, n_1, n_2) = G^l(T, P, n_1^l, n_2^l) + \frac{\partial G^l}{\partial n_1} \left( \frac{\partial n_1}{\partial \delta_1} \right) \delta_1 + \frac{\partial G^l}{\partial n_2} \left( \frac{\partial n_2}{\partial \delta_2} \right) \delta_2$$

$$G^l(T, P, n_1, n_2) = G^l(T, P, n_1^l, n_2^l) + \mu_1(T, P, x_1^l) n_1^s + \mu_2(T, P, x_1^l) n_2^s$$

This equation is combined with equation (II.12) to give

$$\Delta G_{imm}^{\infty} = G^s - \mu_1 n_1^s - \mu_2 n_2^s \quad (\text{II.14})$$

By the same method we find

$$\begin{aligned} \Delta S_{imm}^{\infty} &= S^s - n_1^s \bar{S}_1 - n_2^s \bar{S}_2 \\ \Delta V_{imm}^{\infty} &= V^s - n_1^s \bar{V}_1 - n_2^s \bar{V}_2 \\ \Delta H_{imm}^{\infty} &= H^s - n_1^s \bar{H}_1 - n_2^s \bar{H}_2 \end{aligned} \quad (\text{II.15})$$

where  $\bar{S}_i$  ,  $\bar{V}_i$  ,  $\bar{H}_i$  , and  $\mu_i$  are the partial molar properties of the reference liquid.

### Monolayer Model Equations

In any monolayer theory  $m$ ,  $n_1^s$ ,  $n_2^s$  are related [29] by

$$m = \alpha_1 n_1^s + \alpha_2 n_2^s \quad (\text{II.16})$$

The quantities  $\alpha_1$  and  $\alpha_2$  may or may not be considered constant.  $\alpha_1$  and  $\alpha_2$  can depend on temperature, pressure, and

surface composition in which case  $m=m(T,P,n_1^s,n_2^s)$ . Then  $\alpha_1$  and  $\alpha_2$  are defined as

$$\alpha_1 = \left( \frac{\partial m}{\partial n_1^s} \right)_{T,P,n_2^s} \quad (\text{II.17})$$

$$\alpha_2 = \left( \frac{\partial m}{\partial n_2^s} \right)_{T,P,n_1^s}$$

The total differential for  $m$  is then

$$dm = \left( \frac{\partial m}{\partial T} \right)_{P,n_1^s,n_2^s} dT + \left( \frac{\partial m}{\partial P} \right)_{T,n_1^s,n_2^s} dP + \alpha_1 dn_1^s + \alpha_2 dn_2^s \quad (\text{II.18})$$

To specify a particular monolayer model, one specifies  $m(T,P,n_1^s,n_2^s)$  and obtains  $\alpha_1$  and  $\alpha_2$  from equation (II.17). In our calculation we take

$$m = \frac{1}{a_s(x_1^s, T, P)} (a_1 n_1^s + a_2 n_2^s) \quad (\text{II.19})$$

where  $a_i$  is the surface area covered by one mole of adsorbate  $i$  and  $a_s$  is the surface area per gram of adsorbent. The

expression for  $\alpha_1$  and  $\alpha_2$ , computed from equations (II.17), are

$$\alpha_1 = \left( \frac{\partial m}{\partial n_1^s} \right)_{T, P, n_2^s} = \frac{a_1}{a_s} - \frac{\left( \frac{\partial a_s}{\partial x_1^s} \right)_{T, P}}{a_s^2} x_2^s (a_1 x_1^s + a_2 x_2^s)$$

$$\alpha_2 = \left( \frac{\partial m}{\partial n_2^s} \right)_{T, P, n_1^s} = \frac{a_2}{a_s} + \frac{\left( \frac{\partial a_s}{\partial x_1^s} \right)_{T, P}}{a_s^2} x_1^s (a_1 x_1^s + a_2 x_2^s) \quad (\text{II.20})$$

The quantity  $a_s$  is assumed constant in most theories, but by allowing it to depend on surface composition, one may account for disaggregation or swelling of the adsorbent.

The surface chemical potential, used in monolayer theory, is defined by

$$g_i = \mu_i + u^s \alpha_i \quad (\text{II.21})$$

Using equation (II.21) one may convert equations (II.8), (II.9), and (II.10) to

$$\begin{aligned}
dG^s &= \left( -S^s + u^s \left( \frac{\partial m}{\partial T} \right)_{P, n_1^s, n_2^s} \right) dT + \left( V^s + u^s \left( \frac{\partial m}{\partial P} \right)_{T, n_1^s, n_2^s} \right) dP + g_1 dn_1^s + g_2 dn_2^s \\
G^s &= g_1 n_1^s + g_2 n_2^s \\
0 &= \left( -S^s + u^s \left( \frac{\partial m}{\partial T} \right)_{P, n_1^s, n_2^s} \right) dT + \left( V^s + u^s \left( \frac{\partial m}{\partial P} \right)_{T, n_1^s, n_2^s} \right) dP - n_1^s dg_1 - n_2^s dg_2
\end{aligned}$$

(II.22)

The ideal surface corresponds to choosing the surface chemical potential to have the forms [29]

$$\begin{aligned}
g_i &= g_i^o(T, P) + RT \ln(x_i^s) \\
g_i^o &= \mu_i^o + u_i^{so} \alpha_i^o
\end{aligned} \quad (\text{II.23})$$

where  $\mu_i^o$  is the standard-state chemical potential of  $i$  and  $u_i^{so}$  is the chemical potential of the adsorbent associated with pure liquid component  $i$  and  $\alpha_i^o = \alpha_i$  (at  $x_i^s = 1$ ).

### Patchwise Monolayer Model

We consider the following types of adsorbents.





For the patchwise, heterogeneous adsorbent we define

$Z_a$  = number of A-substituted sites/number of substitution site

$Z_b$  = number of B-substituted sites/number of substitution site

(II.25)

$\bar{m}$  = total mass of adsorbents/total mmoles of substitution site

(II.26)

$a_s(T, P, x_1^s, Z_a)$  = total specific area of adsorbents

(II.27)

We make the assumption that immersing a patchwise adsorbent having  $n_{ss}$  number of substitution sites with  $Z_b$  number of B-substituted sites per number of substitution sites and  $Z_a$  number of A-substituted sites per number of substitution sites is the same as immersing a mixture of adsorbents A and B. It is the same when the number of substituted sites on adsorbent A is equal to  $n_{ss}Z_a$  and the number of substituted sites is on adsorbent B is equal to  $n_{ss}Z_b$ .

The total work of transferring  $dm_a$  and  $dm_b$  from a vacuum to a system of interest is

$$u_a^s dm_a + u_b^s dm_b$$

and the work for transferring the equivalent heterogeneous adsorbent is

$$u^s dm$$

therefore

$$u^s dm = u_a^s dm_a + u_b^s dm_b$$

Integration gives

$$u^s m = u_a^s m_a + u_b^s m_b \quad (\text{II.30})$$

Equations (II.31) and (II.32) follow

$$u^s \bar{m} n_{ss} = u_a^s \bar{m}_a n_{ss} Z_a + u_b^s \bar{m}_b n_{ss} Z_b \quad (\text{II.31})$$

$$u^s \bar{m} = u_a^s \bar{m}_a Z_a + u_b^s \bar{m}_b Z_b \quad (\text{II.32})$$

### Adsorption Isotherm

The adsorption isotherm is a model independent measure of which liquid component is preferentially adsorbed. It is defined by

$$\frac{n_i^o}{m} = \frac{n^o}{m} (x_i^{ol} - x_i^l) = \frac{n^o}{m} \Delta x_i \quad (i=1, 2, \dots) \quad (\text{II.33})$$

Equation (II.33) describes how to obtain  $n_i^o$  from measured values of  $x_i^{ol}$  and  $x_i^l$ .  $n^o$  is the total moles of liquid mixture,  $x_i^{ol}$  is the liquid mole fraction of component  $i$  before adsorption, and  $x_i^l$  is the liquid mole fraction of component  $i$  after adsorption and equilibrium is established.

Next we develop equations to find  $n_i^o$  from a surface model. The following mass balance gives

$$\frac{n^o}{m} x_i^{ol} = \frac{[n_i^s + (n^o - n^s) x_i^l]}{m} = \frac{n_i}{m} \quad (\text{II.34})$$

where  $n^s = n_1^s + n_2^s$ . Using equations (II.33), and (II.34), we have

$$\frac{n_i^o}{m} = \frac{1}{m} [n_i^s - n^s x_i^s] = \frac{n^s}{m} [x_i^s - x_i^l] \quad (\text{II.35})$$

where  $x_i^s = \frac{n_i^s}{n^s}$

Equations (II.33) and (II.35) are the link between theory and physical measurement. Equation (II.33) describes how to obtain  $n_i^o$  from measured  $x_i^{ol}$  and  $x_i^l$ . Equation (II.35) describes how to obtain  $n_i^o$  from theory; to use it we must devise a method in which  $x_i^s$  and  $n^s$  are determined as a function of the measurable  $x_i^l$ . This is done in the following manner.

Equations (II.10) and (II.32) imply

$$\frac{n_1^s}{m} \bar{m} = \frac{n_{a1}^s}{m_a} \bar{m}_a Z_a + \frac{n_{b1}^s}{m_b} \bar{m}_b Z_b \quad (\text{II.36})$$

$$\frac{n_2^s}{m} \bar{m} = \frac{n_{a2}^s}{m_a} \bar{m}_a Z_a + \frac{n_{b2}^s}{m_b} \bar{m}_b Z_b \quad (\text{II.37})$$

One now must determine the quantities  $n_{a1}^s/m_a$ ,  $n_{a2}^s/m_a$ ,  $n_{b1}^s/m_b$ ,  $n_{b2}^s/m_b$ . This is done first by determining  $x_{a1}^s$ ,  $x_{a2}^s$ ,  $x_{b1}^s$ , and  $x_{b2}^s$  as a function of  $x_2^l$ .

Generalization of equation (II.21) gives

$$\begin{aligned} g_{a1} &= \mu_1 + u_a^s \alpha_{a1} \\ g_{a2} &= \mu_2 + u_a^s \alpha_{a2} \end{aligned} \quad (\text{II.38})$$

$$\begin{aligned} g_{b1} &= \mu_1 + u_b^s \alpha_{b1} \\ g_{b2} &= \mu_2 + u_b^s \alpha_{b2} \end{aligned} \quad (\text{II.39})$$

It can be seen from equations (II.38) and (II.39)

$$u_a^s = \frac{g_{a2} - \mu_2}{\alpha_{a2}} = \frac{g_{a1} - \mu_1}{\alpha_{a1}} \quad (\text{II.40})$$

$$u_b^s = \frac{g_{b2} - \mu_2}{\alpha_{b2}} = \frac{g_{b1} - \mu_1}{\alpha_{b1}} \quad (\text{II.41})$$

Using equations (II.23), (II.40), and (II.41) and

$$\mu_i = \mu_i^o + RT \ln(a_i^I) \quad (\text{II.42})$$

we have

$$\frac{1}{\alpha_{a1}} \left[ RT \ln \left( \frac{x_{a1}^s}{a_1^I} \right) + u_{a1}^{so} \alpha_{a1}^o \right] = \frac{1}{\alpha_{a2}} \left[ RT \ln \left( \frac{x_{a2}^s}{a_2^I} \right) + u_{a2}^{so} \alpha_{a2}^o \right] \quad (\text{II.43})$$

$$\frac{1}{\alpha_{b1}} \left[ RT \ln \left( \frac{x_{b1}^s}{a_1^I} \right) + u_{b1}^{so} \alpha_{b1}^o \right] = \frac{1}{\alpha_{b2}} \left[ RT \ln \left( \frac{x_{b2}^s}{a_2^I} \right) + u_{b2}^{so} \alpha_{b2}^o \right] \quad (\text{II.44})$$

Equations (II.43) and (II.44) can not be solved analytically,

they must be solved iteratively, determining  $x_{a1}^s(x_2^l)$ ,  $x_{a2}^s(x_2^l)$ ,  $x_{b1}^s(x_2^l)$ , and  $x_{b2}^s(x_2^l)$ .

In order to deal with equations (II.43) and (II.44), the non-ideality of the bulk solution must be accounted for. This is done by determining the activity coefficients via Wilson equations and well established Wilson parameters [30].

$$\begin{aligned} \gamma_1^l &= \exp \left\{ -\ln(x_1^l + x_2^l G_{21}) - \left[ \frac{x_1^l}{x_1^l + x_2^l G_{21}} + \frac{x_2^l G_{12}}{x_1^l G_{12} + x_2^l} \right] + 1 \right\} \\ \gamma_2^l &= \exp \left\{ -\ln(x_1^l G_{12} + x_2^l) - \left[ \frac{x_1^l G_{21}}{x_1^l + x_2^l G_{21}} + \frac{x_2^l}{x_1^l G_{12} + x_2^l} \right] + 1 \right\} \end{aligned} \quad (\text{II.45})$$

where

$$G_{ji} = \left( \frac{V_j}{V_i} \right) \exp\{-\tau_{ji}\} \quad (\text{II.46})$$

Here  $V_i$  is the molar volume of component  $i$  and  $\tau_{ji}$  are the temperature dependent parameters which are varied to match measured thermodynamic properties.

The quantities  $n_{ai}^s/m_a$  and  $n_{bi}^s/m_b$  required in equations (II.36) and (II.37) are obtained from [c. f. Eq.(II.16)]

$$\frac{m_a}{n_a^s} = \alpha_{a1} X_{a1}^s + \alpha_{a2} X_{a2}^s \quad (\text{II.47})$$

$$\frac{m_b}{n_b^s} = \alpha_{b1} X_{b1}^s + \alpha_{b2} X_{b2}^s \quad (\text{II.48})$$

and

$$\begin{aligned} \frac{n_{a1}^s}{m_a} &= \frac{n_a^s}{m_a} X_{a1}^s \\ \frac{n_{a2}^s}{m_a} &= \frac{n_a^s}{m_a} X_{a2}^s \end{aligned} \quad (\text{II.49})$$

$$\begin{aligned} \frac{n_{b1}^s}{m_b} &= \frac{n_b^s}{m_b} X_{b1}^s \\ \frac{n_{b2}^s}{m_b} &= \frac{n_b^s}{m_b} X_{b2}^s \end{aligned} \quad (\text{II.50})$$

Equations (II.36) and (II.37) give  $n_1^s/m$  and  $n_2^s/m$ , and  $n^s$  and  $x_i^s$  are determined from

$$\frac{n^s}{m} = \frac{n_1^s}{m} + \frac{n_2^s}{m} \quad (\text{II.51})$$

$$x_i^s = \frac{n_i^s}{n^s} \quad (\text{II.52})$$

With these quantities equation (II.35) gives the excess isotherm as a function of  $x_i^l$ .

### Heat of immersion

Another measurable quantity is the heat of immersion,  $\Delta H_{\text{imm}}^s$ , which is expressed in equation (II.15) in terms of the surface enthalpy  $H^s$  and the partial molar enthalpies  $H_1$  and  $H_2$  of the bulk solution.

The following equations describe  $H^s$ . From the first of equations (II.22) we have

$$\left( \frac{\partial G^s}{\partial T} \right)_{P, n_1^s, n_2^s} = -S^s + U^s \left( \frac{\partial m}{\partial T} \right)_{P, n_1^s, n_2^s} \quad (\text{II.53})$$

And from the second of equations (II.22) we have

$$\left( \frac{\partial G^s}{\partial T} \right)_{P, n_1^s, n_2^s} = n_1^s \left( \frac{\partial g_1}{\partial T} \right)_{P, n_1^s, n_2^s} + n_2^s \left( \frac{\partial g_2}{\partial T} \right)_{P, n_1^s, n_2^s} \quad (\text{II.54})$$

therefore



$$S^s = -n_1^s \left( \frac{\partial g_1}{\partial T} \right)_{P, n_1^s, n_2^s} - n_2^s \left( \frac{\partial g_2}{\partial T} \right)_{P, n_1^s, n_2^s} + u^s \left( \frac{\partial m}{\partial T} \right)_{P, n_1^s, n_2^s} \quad (\text{II.55})$$

The quantity  $H^s$  maybe written as

$$H^s = G^s + TS^s \quad (\text{II.56})$$

Using equations (II.22), (II.55), and (II.56) one gets

$$H^s = n_1^s \left\{ g_1 - T \left( \frac{\partial g_1}{\partial T} \right)_{P, n_1^s, n_2^s} \right\} + n_2^s \left\{ g_2 - T \left( \frac{\partial g_2}{\partial T} \right)_{P, n_1^s, n_2^s} \right\} + T u^s \left( \frac{\partial m}{\partial T} \right)_{P, n_1^s, n_2^s} \quad (\text{II.57})$$

it can be shown that

$$g_i - T \left( \frac{\partial g_i}{\partial T} \right)_{P, n_i^s, n_{i+1}^s} = \left( \frac{\partial g_i / T}{\partial 1/T} \right)_{P, n_i^s, n_{i+1}^s} \quad (\text{II.58})$$

so

$$H^s = n_1^s \left( \frac{\partial g_1 / T}{\partial 1/T} \right)_{P, n_1^s, n_2^s} + n_2^s \left( \frac{\partial g_2 / T}{\partial 1/T} \right)_{P, n_1^s, n_2^s} + T u^s \left( \frac{\partial m}{\partial T} \right)_{P, n_1^s, n_2^s} \quad (\text{II.59})$$

Equations (II.21), (II.23), and (II.42), give

$$\left(\frac{\partial g_i/T}{\partial 1/T}\right)_{P, n_i^s, n_{i+1}^s} = \left(\frac{\partial \mu_i^0/T}{\partial 1/T}\right)_{P, n_i^s, n_{i+1}^s} + \left(\frac{\partial \{\alpha_i^0 u_i^{s0}/T\}}{\partial 1/T}\right)_{P, n_i^s, n_{i+1}^s}$$

(II.60)

which gives

$$\left(\frac{\partial g_i/T}{\partial 1/T}\right)_{P, n_i^s, n_{i+1}^s} = \bar{H}_i^0 + \left(\frac{\partial \{\alpha_i^0 u_i^{s0}/T\}}{\partial 1/T}\right)_{P, n_i^s, n_{i+1}^s} \quad (\text{II.61})$$

where  $\frac{\partial \mu_i^0/T}{\partial 1/T} = \bar{H}_i^0$

The partial molar enthalpy  $\bar{H}_i$  of the bulk liquid is related to the activity coefficient by

$$\bar{H}_i = \left(\frac{\partial \mu_i/T}{\partial 1/T}\right)_{P, x_i^l} = \left(\frac{\partial \mu_i^0/T}{\partial 1/T}\right)_P + R \left(\frac{\partial \ln \gamma_i^l}{\partial 1/T}\right)_{P, x_i^l} \quad (\text{II.62})$$

or

$$\bar{H}_i = \bar{H}_i^0 + RTW_i^l$$

where  $W_i^l = \frac{1}{T} \left(\frac{\partial \ln \gamma_i^l}{\partial 1/T}\right)_{P, x_i^l}$  (II.63)

It follows from equation (II.45)--the Wilson equations--that the temperature coefficients are

$$w_1^I = \frac{x_2^I \tau'_{21} G_{21} + x_2^I \tau'_{12} G_{12}}{x_1^I + x_2^I G_{21}} - \frac{x_1^I x_2^I \tau'_{21} G_{21}}{(x_1^I + x_2^I G_{21})^2} - \frac{x_1^I x_2^I \tau'_{12} (G_{12})^2}{(x_1^I G_{12} + x_2^I)^2} \quad (\text{II.64})$$

$$w_2^I = \frac{x_1^I \tau'_{12} G_{12} + x_1^I \tau'_{21} G_{21}}{x_1^I G_{12} + x_2^I} - \frac{x_1^I x_2^I \tau'_{21} (G_{21})^2}{(x_1^I + x_2^I G_{21})^2} - \frac{x_1^I x_2^I \tau'_{12} G_{12}}{(x_1^I G_{12} + x_2^I)^2} \quad (\text{II.64})$$

where

$$\tau'_{ij} = \left( \frac{1}{T} \right) \frac{\partial \tau_{ij}}{\partial 1/T} \quad (\text{II.65})$$

In order to determine  $w_1^I$  and  $w_2^I$  we must determine the values for  $\tau'_{12}$  and  $\tau'_{21}$  from experimental heats of mixing as follows. Since

$$\Delta G^{mix} = RT [x_1^I \ln(\gamma_1^I x_1^I) + x_2^I \ln(\gamma_2^I x_2^I)] \quad (\text{II.66})$$

it follows that

$$\Delta H^{mix} = \frac{\partial(\Delta G^{mix}/T)}{\partial 1/T} = R \left[ x_1^I \frac{\partial \ln(\gamma_1^I)}{\partial 1/T} + x_2^I \frac{\partial \ln(\gamma_2^I)}{\partial 1/T} \right]$$

or

$$\Delta H^{mix} = RT (x_1^I w_1^I + x_2^I w_2^I) \quad (\text{II.67})$$

Using equations (II.46), (II.64), and (II.67), we vary the values of  $r_{12}'$  and  $r_{21}'$  until a good fit with the experimental data is obtained.

We are now ready to develop the equation for the heat of immersion. From equations (II.59), (II.61) and (II.15)

$$\Delta H_{imm}^{\infty} = n_1^s \left\{ \left( \frac{\partial(\alpha_1^o u_1^{so}/T)}{\partial 1/T} \right)_{P, n_1^s, n_2^s} - RTw_1^l \right\} + n_2^s \left\{ \left( \frac{\partial(\alpha_2^o u_2^{so}/T)}{\partial 1/T} \right)_{P, n_1^s, n_2^s} - RTw_2^l \right\} +$$

$$Tu^s \left( \frac{\partial m}{\partial T} \right)_{P, n_1^s, n_2^s}$$

(II.68)

From equation (II.16) we obtain

$$\left( \frac{\partial m}{\partial T} \right)_{P, n_1^s, n_2^s} = n_1^s \left( \frac{\partial \alpha_1}{\partial T} \right)_{P, n_1^s, n_2^s} + n_2^s \left( \frac{\partial \alpha_2}{\partial T} \right)_{P, n_1^s, n_2^s}$$

(II.69)

Using equations (II.68) and (II.69) we obtain a working expression for the heat of immersion.

$$\Delta H_{imm}^{\infty} = n_1^s \left\{ \left( \frac{\partial(\alpha_1^o u_1^{so}/T)}{\partial 1/T} \right)_{P, n_1^s, n_2^s} + u^s T \left( \frac{\partial \alpha_1}{\partial T} \right)_{P, n_1^s, n_2^s} - RTw_1^l \right\} +$$

$$n_2^s \left\{ \left( \frac{\partial(\alpha_2^o u_2^{so}/T)}{\partial 1/T} \right)_{P, n_1^s, n_2^s} + u^s T \left( \frac{\partial \alpha_2}{\partial T} \right)_{P, n_1^s, n_2^s} - RTw_2^l \right\}$$

(II.70)

For the A-type and B-type adsorbents we write

$$\Delta H_{imm}^{\infty} = n_{a1}^s \left\{ \left( \frac{\partial(\alpha_{a1}^o u_{a1}^{so}/T)}{\partial 1/T} \right)_{P, n_{a1}^s, n_{a2}^s} + u_a^s T \left( \frac{\partial \alpha_{a1}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} - RTw_1^1 \right\} +$$

$$n_{a2}^s \left\{ \left( \frac{\partial(\alpha_{a2}^o u_{a2}^{so}/T)}{\partial 1/T} \right)_{P, n_{a1}^s, n_{a2}^s} + u_a^s T \left( \frac{\partial \alpha_{a2}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} - RTw_2^1 \right\}$$

(II.71)

$$\Delta H_{imm}^{\infty} = n_{b1}^s \left\{ \left( \frac{\partial(\alpha_{b1}^o u_{b1}^{so}/T)}{\partial 1/T} \right)_{P, n_{b1}^s, n_{b2}^s} + u_b^s T \left( \frac{\partial \alpha_{b1}}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} - RTw_1^1 \right\} +$$

$$n_{b2}^s \left\{ \left( \frac{\partial(\alpha_{b2}^o u_{b2}^{so}/T)}{\partial 1/T} \right)_{P, n_{b1}^s, n_{b2}^s} + u_b^s T \left( \frac{\partial \alpha_{b2}}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} - RTw_2^1 \right\}$$

(II.72)

Equation(II.10), (II.15), and (II.32) imply the following form for the patchwise, heterogeneous adsorbent

$$H_{imm}^{\infty} = Z_a \overline{m}_a H_{imma} + Z_b \overline{m}_b H_{immb} \quad (II.73)$$

If one assumes the specific surface area  $a_s$  is temperature independent, then it follows from equation (II.20) that the  $\alpha$ 's are temperature independent. In this case equation (II.70) reduces to

$$\Delta H_{imm}^{\infty} = n_1^s \left\{ \alpha_1 \left( \frac{\partial u_1^{so}/T}{\partial 1/T} \right)_{P, n_1^s, n_2^s} - RTw_1^1 \right\} + n_2^s \left\{ \alpha_2 \left( \frac{\partial u_2^{so}/T}{\partial 1/T} \right)_{P, n_1^s, n_2^s} - RTw_2^1 \right\}$$

(II.74)

### III. Results for Illites

In the first series of calculations we model isotherms and heats of adsorption measured by Dekany [19][21]. The illites varied from a non-sustituted illite (Na-illite), whose surface is polar, to an illite (illite-5), whose surface is made completely non-polar by substituting Na+ for HDP+ (hexadecyl-pyridinium cation) and covering the remaining surface by DS(dodecyl sulfate anion). Intermediate illites (illites 1, 2, and 3) are partially substituted.

We compute the parameters  $\bar{m}_a$ ,  $\bar{m}_b$ , and  $\bar{m}$ , defined in equations (II.24) and (II.26) as follows. Adsorbent B is Na-illite and adsorbent A is illite-5. Illite-5 was totally substituted with 0.233 mmoles of HDP+ cation and 0.016 mmoles of DS anion per gram of Na-illite. Hence  $\bar{m}_b$  is given by

$$\frac{1}{\bar{m}_b} = 0.233 (\text{mmoles/g}) + 0.016 (\text{mmole/g}) \quad (\text{III.1})$$

When 1.000g of Na-illite (adsorbent B) is converted to illite-5 (adsorbent A), 0.233 mmoles of Na+ is removed, 0.233 mmoles of HDP+ cation is added, and 0.016 mmoles of DS anion is added; therefore

$$\bar{m}_a = \frac{1.000 - 0.233 \times 10^{-3} (MW_{Na}) + 0.233 \times 10^{-3} (MW_{HDP}) + 0.016 (MW_{DS})}{0.233 + 0.016} \quad (\text{III.2})$$

where MW denotes molecular weight. Values of  $\bar{m}_a$  and  $\bar{m}_b$  are thus  $\bar{m}_b = 4.016 \text{ g/mmole}$  and  $\bar{m}_a = 4.308 \text{ g/mmole}$ . For illite-1, 0.097mmoles of HDP+ replace Na+ per gram of the original illite-1; therefore

$$Z_a = \frac{0.097}{0.233 + 0.016} = 0.39 \quad (\text{III.3})$$

The  $Z_a$ 's for illite-2 and illite-3 are computed similarly. In each case we obtain  $Z_b$  from

$$Z_a + Z_b = 1 \quad (\text{III.4})$$

To compute  $\bar{m}$  for illites 1, 2, and 3 we use

$$\bar{m} = \frac{1.000 + \left[ \frac{\text{mmole HDP+}}{\text{grams Na-illite}} \right] \times 10^{-3} \frac{\text{mole}}{\text{mmole}} \times [MW_{\text{HDP+}} - MW_{\text{Na+}}] (\text{g/mole})}{0.233 (\text{mmole/g}) + 0.016 (\text{mmole/g})}$$

$$\text{so } \bar{m} = \bar{m}_b + Z_a \times [MW_{\text{HDP+}} - MW_{\text{Na+}}]$$

$$(\text{III.15})$$

The areas  $a_1$  and  $a_2$  were calculated from the area of benzene and methanol; we used the values calculated by Dekany et al [17]. The Wilson parameters  $V_1$ ,  $V_2$ ,  $\tau_{12}$ , and  $\tau_{21}$  were obtained from Prausnitz [30]. Other Wilson parameters,  $\tau_{12}'$  and  $\tau_{21}'$ , we obtained by fitting equation (II.67) to heat of mixing data [31]. Table III.1 contains all the above-mentioned parameters.

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Table III.1      Parameters used in all illite models

$r_{12}=3.104$		$Z_a$	$Z_b$
$r_{21}=0.243$	Na-illite	0	1
$V_1^l = 90.5\text{cm}^3/\text{mole}$	illite-1	0.39	0.61
$V_2^l = 41.1\text{cm}^3/\text{mole}$	illite-2	0.56	0.44
$a_1=180\text{m}^2/\text{mmole}$	illite-3	0.94	0.06
$a_2=95\text{m}^2/\text{mmole}$	illite-5	1	0
$r_{12}' = 1.5$			
$r_{21}' = 1.1$			

---

#### Model 1

In model 1 the specific surface areas  $a_s$ --and hence the  $\alpha_i$ 's--are constant. Thus swelling and disaggregation are not taken into account.



Table III.2 Parameters used for model 1 isotherms

	$a_{sa}$	$a_{sb}$	$u_{a1}^{so}$	$u_{a2}^{so}$	$u_{b1}^{so}$	$u_{b2}^{so}$
	(m <sup>2</sup> /g)	(m <sup>2</sup> /g)	(J/g)	(J/g)	(J/g)	(J/g)
Na-illite	0	150	0	0	1	-3
illite-1	120	150	-3	1.5	1	-3
illite-2	120	150	-3	1.5	1	-3
illite-3	120	150	-3	1.5	1	-3
illite-5	120	0	-3	1.5	0	0

### Isotherms

The following parameters were obtained by fitting equation (II.35) to the experimental isotherms of Na-illite [21]:  $a_{sb}$ ,  $u_{b1}^{so}$ ,  $u_{b2}^{so}$ . In the same way,  $a_{sa}$ ,  $u_{a1}^{so}$ , and  $u_{a2}^{so}$  were obtained from the illite-5 isotherm. Figs. 4 and 8 show the fits (points represents experiment, solid lines are theory). These values were then used to predict the remaining illite isotherms 1, 2, and 3 (Figs. 5, 6, and 7). Table III.2 contains these parameter values.

Figs. 1 through 3 (Na-illite, illite-2, and illite-5 respectively) indicate the nature of the adsorption according to this model. They are theoretical plots of  $x_2^s$  as a function of  $x_2^l$ . The bisecting line represents the values at which  $x_2^l = x_2^s$ , the azeotrope point. It is seen from Fig. 1 that

component 2 (methanol) is always preferentially adsorbed onto the polar surface of Na-illite--a reasonable result. Intuitively, one would expect component 1 (benzene) to be preferentially adsorbed at all compositions on the non-polar illite-5, but Fig. 3 shows component 2 (methanol) is preferentially adsorbed at low  $x_2^l$ . According to the model this occurs because of the non-ideality of the bulk solution. Fig. 2 shows that on a heterogeneous surface component 2 is preferentially adsorbed at low  $x_2^l$  and that component 1 is preferentially adsorbed for large  $x_2^l$ .

Examining the overall fits (Figs. 4 through 8), we see a good fit for the Na-illite. For illites 1 and 2 (Figs. 5 and 6) the model predicts an inadequate amount of methanol adsorption when methanol is the minor liquid component in solution and an inadequate amount of benzene adsorption when benzene is the minor liquid component in solution. In the case of illite-3 (Fig. 7) the model predicts an excessive amount of methanol adsorption through most of the concentration range. The model predicts, in the case of the totally saturated illite-5, an excessive amount of benzene adsorption when benzene is the minor liquid component in solution. The values of the "sticking" parameters are reasonable. The positive value of  $u_{b1}^{so}$  and the negative value of  $u_{b2}^{so}$  means component 2 (methanol) is more firmly attached to adsorbent B (Na-illite) than is component 1 (benzene). ( $u_{bi}^{so}$  is the free energy change associated with immersing adsorbent B

in pure i--for fixed  $T, P, n_1, n_2$ .) Similarly, the negative value of  $u_{a1}^{so}$  and the positive value of  $u_{a2}^{so}$  corresponds to component 1 (benzene) being more firmly attached to the non-polar adsorbent A (illite-5) than component 2 (methanol).

## Heat

We fit equation (II.74) to experimental heats of immersion [21] of Na-illite (Fig. 15), using  $\partial(u_{b1}^{so}/T)/\partial(1/T)$  and  $\partial(u_{b2}^{so}/T)/\partial(1/T)$  as fitting parameters. Then we find  $\partial(u_{a1}^{so}/T)/\partial(1/T)$  and  $\partial(u_{a2}^{so}/T)/\partial(1/T)$  by fitting illite-3 data (heat data for illite-5 is not available). Values are listed in Table III.3. Figs. 16 and 17 show predictions for illites 1 and 2 based on the Table III.3 values.

The fits are not good. Theory gives a spurious spike at low  $x_2^l$  for Na-illite (Fig. 15). It is due to the non-ideality of the solution: heat is released when adsorption of component 2 contributes to the solution's demixing. This can be seen in Fig. 11, which shows the "bulk" and the "surface" contributions to equation (II.74) separately. A similar theoretical spike at large  $x_2^l$  develops with increasing organophilicity (Figs. 16, 17, 18) due to demixing when benzene is adsorbed. Resolutions of the heats of illites 1, 2, and 3 into surface and bulk contributions are shown in Figs. 12, 13 and 14.

---

Table III.3 Heat parameters for Illite-model 1

	$\partial(u_{b1}^{so}/T)/\partial(1/T)$	$\partial(u_{b2}^{so}/T)/\partial(1/T)$
Na-illite	-9	-14
illite-1	-9	-14
illite-2	-9	-14
illite-3	-9	-14
	$\partial(u_{a1}^{so}/T)/\partial(1/T)$	$\partial(u_{a2}^{so}/T)/\partial(1/T)$
Na-illite	0	0
illite-1	-4.0	-3.5
illite-2	-4.0	-3.5
illite-3	-4.0	-3.5

---

In conclusion, the illite data cannot be satisfactorily fit with this model. If one takes non-ideality of the bulk solution into account, then large, exothermic peaks are predicted which are not found experimentally. Evidently there must be compensating endothermic effects that the model does not take into account.

#### Model 2

In model 2  $a_{sa}$  and  $a_{sb}$  are allowed to vary with surface composition and temperature. Our picture is this: When the polar surface of adsorbent B is immersed in the non-polar

component 1, the surface area for adsorption will be at a minimum because the adsorbent will tend to aggregate. Adding polar component 2 will cause the adsorbent to disaggregate as the polar component 2 strongly adsorbs to the polar adsorbent: thus  $a_{sb}$  increases with increasing  $x_{2b}^s$ . This introduces an endothermic effect that compensates for the exothermic demixing of the bulk solution.

We assume in this section that  $a_{sa}$  and  $a_{sb}$  are linear functions of  $x_{a1}^s$  and  $x_{b1}^s$  respectively:

$$a_{sa}(x_{a1}^s, T, P) = M_a x_{a1}^s + b_a \quad (\text{III.6})$$

$$a_{sb}(x_{b1}^s, T, P) = M_b x_{b1}^s + b_b \quad (\text{III.7})$$

Application of equation (II.20) to surfaces A and B gives

$$\begin{aligned} \alpha_{a1} &= \left( \frac{\partial m_a}{\partial n_{a1}^s} \right)_{P, T, n_{a2}^s} = \frac{a_1}{a_{sa}} - \frac{\left( \frac{\partial a_{sa}}{\partial x_{a1}^s} \right)_{T, P}}{a_{sa}^2} x_{a2}^s (a_1 x_{a1}^s + a_2 x_{a2}^s) \\ \alpha_{a2} &= \left( \frac{\partial m_a}{\partial n_{a2}^s} \right)_{P, T, n_{a1}^s} = \frac{a_2}{a_{sa}} + \frac{\left( \frac{\partial a_{sa}}{\partial x_{a1}^s} \right)_{P, T}}{a_{sa}^2} x_{a1}^s (a_1 x_{a1}^s + a_2 x_{a2}^s) \end{aligned} \quad (\text{III.8})$$

where

$$\alpha_{b1} = \left( \frac{\partial m_b}{\partial n_{b1}^s} \right)_{T, P, n_{b2}^s} = \frac{a_1}{a_{sb}} - \frac{\left( \frac{\partial a_{sb}}{\partial x_{b1}^s} \right)_{T, P}}{a_{sb}^2} x_{b2}^s (a_1 x_{b1}^s + a_2 x_{b2}^s) \quad (\text{III.9})$$

$$\alpha_{b2} = \left( \frac{\partial m_b}{\partial n_{b2}^s} \right)_{T, P, n_{b1}^s} = \frac{a_2}{a_{sb}} + \frac{\left( \frac{\partial a_{sb}}{\partial x_{b1}^s} \right)_{T, P}}{a_{sb}^2} x_{b1}^s (a_1 x_{b1}^s + a_2 x_{b2}^s)$$

$$M_a = \left( \frac{\partial a_{sa}}{\partial x_{a1}^s} \right)_{T, P} \quad M_b = \left( \frac{\partial a_{sb}}{\partial x_{b1}^s} \right)_{T, P} \quad (\text{III.10})$$

The parameters  $M_a$ ,  $b_a$ ,  $M_b$ , and  $b_b$ --along with  $u_{a1}^{so}$ ,  $u_{a2}^{so}$ ,  $u_{b1}^{so}$ ,  $u_{b2}^{so}$ --are found by fitting equation (II.35) to the experimental isotherm of Na-illite and illite-5. During the fitting process equations (II.43) and (II.44) are solved for  $x_{a1}^s$  ( $x_2^l$ ) and  $x_{b1}^s$  ( $x_2^l$ ). In some instances we find multiple solutions, which introduces a complication not encountered in the previous model.

The thermodynamically correct solution is the solution that occurs at the absolute minimum on the  $G(n_1^s, n_2^s)$  surface ( $T, P, m, n_1$ , and  $n_2$  are fixed) when constrained to the "monolayer" condition. Now according to equation (II.7),

$$G = G^l(n_1 - n_1^s, n_2 - n_2^s, T, P) + A^c(T, m) + G^s(n_1^s, n_2^s, T, P) \quad (\text{III.11})$$

which becomes, with the use of equation (II.9)

$$G = n_1 \mu_1 + n_2 \mu_2 + A^c + u^s m \quad (\text{III.12})$$

Only the last term varies with  $n_1^s$  and  $n_2^s$ , so the minimum in  $G$  corresponds to the minimum in  $u^s$ . Thus we select the correct solution by comparing values of  $u^s$ , which are computed

through equations (II.40) and (II.41).

Best fits to the isotherms of Na-illite and illite-5 are shown in Figs. 19 and 23. Corresponding parameters are in Table III.4. Predictions for illites 1, 2, and 3 are given in Figs. 20, 21, and 22.

Table III.4 Parameters for model 2 isotherms

	$u_{b1}^{so}$	$u_{b2}^{so}$	$u_{a1}^{so}$	$u_{a2}^{so}$	$M_b$	$b_b$	$M_a$	$b_a$
Na-illite	1.4	-0.3	0	0	-122	170	0	0
illite-1	1.4	-0.3	-0.4	0.4	-122	170	170	15
illite-2	1.4	-0.3	-0.4	0.4	-122	170	170	15
illite-3	1.4	-0.3	-0.4	0.4	-122	170	170	15
illite-5	0	0	-0.4	0.4	0	0	170	15

Fig. 29 shows  $a_{sb}(x_{b1}^s)$  for the best-fit parameters  $M_b$  and  $b_b$ ; it corresponds to the aggregation of the non-polar adsorbent B (Na-illite) with the enrichment of benzene in solution. Fig. 30 shows  $a_{sa}(x_{a1}^s)$  for the best-fit parameters  $M_a$  and  $b_a$ . The increasing surface area of adsorbent A with increasing  $x_{a1}^s$  predicts the disaggregation of adsorbent A with the enrichment of benzene in solution.

As in model 1, model 2 also produces realistic "sticking" parameters.

## Heats for model 2

We fit equations (II.71) and (II.72) to the experimental heats of Na-illite and illite-3. The quantities

$$\left( \frac{\partial \alpha_i^0 u_i^{s0} / T}{\partial 1/T} \right) \quad (\text{III.13})$$

we treat as fitting parameters and

$$\left( \frac{\partial \alpha_i}{\partial T} \right)_{P, n_i^s, n_{i+1}^s} \quad (\text{III.14})$$

we reduce as follows. From equations (II.20) we find

$$\begin{aligned} & \left( \frac{\partial \alpha_{a1}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} = - \frac{a_1}{a_{sa}^2} \left( \frac{\partial a_{sa}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} \\ & -x_{a2}^s (a_1 x_{a1}^s + a_2 x_{a2}^s) \left[ \frac{\frac{\partial}{\partial T} \left[ \left( \frac{\partial a_{sa}}{\partial x_{a1}^s} \right)_{T, P} \right]_{P, n_{a1}^s, n_{a2}^s} a_{sa} - 2 \left( \frac{\partial a_{sa}}{\partial x_{a1}^s} \right)_{T, P} \left( \frac{\partial a_{sa}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s}}{a_{sa}^3} \right] \\ & \left( \frac{\partial \alpha_{a2}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} = - \frac{a_2}{a_{sa}^2} \left( \frac{\partial a_{sa}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} \\ & +x_{a1}^s (a_1 x_{a1}^s + a_2 x_{a2}^s) \left[ \frac{\frac{\partial}{\partial T} \left[ \left( \frac{\partial a_{sa}}{\partial x_{a1}^s} \right)_{P, T} \right]_{P, n_{a1}^s, n_{a2}^s} a_{sa} - 2 \left( \frac{\partial a_{sa}}{\partial x_{a1}^s} \right)_{P, T} \left( \frac{\partial a_{sa}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s}}{a_{sa}^3} \right] \end{aligned} \quad (\text{III.15})$$



$$\begin{aligned}
& \left( \frac{\partial \alpha_{b1}}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} = - \frac{a_1}{a_{sb}^2} \left( \frac{\partial a_{sb}}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} \\
& -x_{b2}^s (a_1 x_{b1}^s + a_2 x_{b2}^s) \left[ \frac{\frac{\partial}{\partial T} \left[ \left( \frac{\partial a_{sb}}{\partial x_{b1}^s} \right)_{T, P} \right]_{P, n_{b1}^s, n_{b2}^s} a_{sb} - 2 \left( \frac{\partial a_{sb}}{\partial x_{b1}^s} \right)_{T, P} \left( \frac{\partial a_{sb}}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s}}{a_{sb}^3} \right] \\
& +x_{b1}^s (a_1 x_{b1}^s + a_2 x_{b2}^s) \left[ \frac{\frac{\partial}{\partial T} \left[ \left( \frac{\partial a_{sb}}{\partial x_{b1}^s} \right)_{P, T} \right]_{P, n_{b1}^s, n_{b2}^s} a_{sb} - 2 \left( \frac{\partial a_{sb}}{\partial x_{b1}^s} \right)_{P, T} \left( \frac{\partial a_{sb}}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s}}{a_{sb}^3} \right]
\end{aligned}$$

(III.15)

where

$$\begin{aligned}
\left( \frac{\partial a_{sa}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} &= \left( \frac{\partial M_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} x_{a1}^s + \left( \frac{\partial b_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} \\
\left( \frac{\partial a_{sb}}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} &= \left( \frac{\partial M_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} x_{b1}^s + \left( \frac{\partial b_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s}
\end{aligned}$$

(III.16)

We specify the following conditions, which correspond to the assumption that  $a_s$  is temperature independent in the state of maximum disaggregation (pure component 2 for adsorbent B and pure component 1 for adsorbent A).

$$\begin{aligned}\left(\frac{\partial a_{sb}}{\partial T}\right)_{P, n_{b1}^s, n_{b2}^s} &= 0 \quad @ \quad x_{b1}^s = 0 \\ \left(\frac{\partial a_{sa}}{\partial T}\right)_{P, n_{a1}^s, n_{a2}^s} &= 0 \quad @ \quad x_{a1}^s = 1\end{aligned}$$

It follows that

$$\begin{aligned}0 &= \frac{\partial M_a}{\partial T} + \frac{\partial b_a}{\partial T} \\ 0 &= \frac{\partial b_b}{\partial T}\end{aligned} \tag{III.17}$$

and therefore

$$\begin{aligned}\left(\frac{\partial a_{sa}}{\partial T}\right)_{P, n_{a1}^s, n_{a2}^s} &= \left(\frac{\partial b_a}{\partial T}\right)_{P, n_{a1}^s, n_{a2}^s} x_{a2}^s \\ \left(\frac{\partial a_{sb}}{\partial T}\right)_{P, n_{b1}^s, n_{b2}^s} &= \left(\frac{\partial M_b}{\partial T}\right)_{P, n_{b1}^s, n_{b2}^s} x_{b1}^s\end{aligned} \tag{III.18}$$

From equation (III.10), equation (III.19) is obtained.

$$\begin{aligned}\frac{\partial}{\partial T} \left[ \left( \frac{\partial a_{sb}}{\partial x_{b1}^s} \right)_{T, P} \right]_{P, n_{b1}^s, n_{b2}^s} &= \left( \frac{\partial M_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} \\ \frac{\partial}{\partial T} \left[ \left( \frac{\partial a_{sa}}{\partial x_{a1}^s} \right)_{T, P} \right]_{P, n_{a1}^s, n_{a2}^s} &= \left( \frac{\partial M_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} = - \left( \frac{\partial b_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s}\end{aligned} \tag{III.19}$$

Substitution of equations (III.17), (III.18), and (III.19) into equation (III.15) gives equations (III.20).

$$\begin{aligned}
\left(\frac{\partial \alpha_{a1}}{\partial T}\right)_{P, n_{a1}^s, n_{a2}^s} &= \left(\frac{\partial b_a}{\partial T}\right)_{P, n_{a1}^s, n_{a2}^s} x_{a2}^s \left\{ -\frac{a_1}{a_{sa}^2} + (a_1 x_{a1}^s + a_2 x_{a2}^s) \left[ \frac{a_{sa} + 2M_a x_{a2}^s}{a_{sa}^3} \right] \right\} \\
\left(\frac{\partial \alpha_{a2}}{\partial T}\right)_{P, n_{a1}^s, n_{a2}^s} &= -\left(\frac{\partial b_a}{\partial T}\right)_{P, n_{a1}^s, n_{a2}^s} \left\{ \frac{a_2 x_{a2}^s}{a_{sa}^2} + x_{a1}^s (a_1 x_{a1}^s + a_2 x_{a2}^s) \left[ \frac{a_{sa} + 2M_a x_{a2}^s}{a_{sa}^3} \right] \right\} \\
\left(\frac{\partial \alpha_{b1}}{\partial T}\right)_{P, n_{b1}^s, n_{b2}^s} &= -\left(\frac{\partial M_b}{\partial T}\right)_{P, n_{b1}^s, n_{b2}^s} \left\{ \frac{a_1 x_{b1}^s}{a_{sb}^2} + x_{b2}^s (a_1 x_{b1}^s + a_2 x_{b2}^s) \left[ \frac{a_{sb} - 2M_b x_{b1}^s}{a_{sb}^3} \right] \right\} \\
\left(\frac{\partial \alpha_{b2}}{\partial T}\right)_{P, n_{b1}^s, n_{b2}^s} &= \left(\frac{\partial M_b}{\partial T}\right)_{P, n_{b1}^s, n_{b2}^s} x_{b1}^s \left\{ -\frac{a_2}{a_{sb}^2} + (a_1 x_{b1}^s + a_2 x_{b2}^s) \left[ \frac{a_{sb} - 2M_b x_{b1}^s}{a_{sb}^3} \right] \right\}
\end{aligned}$$

(III.20)

The best fits to the Na-illite and illite-3 are shown in Figs. 24 and 27, and the corresponding parameters are listed in Table III.5. Predictions for illites 1 and 2 are shown in Figs. 25 and 26.

### Discussion of Model 2

The multiple solutions of the isotherm equations (II.43) and (II.44) correspond to abrupt changes in adsorption character. For Na-illite a transition occurs at  $x_2^l = 0.048$  where there is a discontinuous change in  $x_2^s$  from 0.005 to

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Table III.5      Parameters    for model 2 heats

	$\partial(u_{b1}^{so}\alpha_{b1}^o/T)/\partial(1/T)$	$\partial(u_{b2}^{so}\alpha_{b1}^o/T)/\partial(1/T)$	$\partial M_b/dT$
Na-illite	-30.0	-6.0	0.5
illite-one	-30.0	-6.0	0.5
illite-two	30.0	-6.0	0.5
illite-three	-30.0	-6.0	0.5

	$\partial(u_{a1}^{so}\alpha_{a1}^o/T)/\partial(1/T)$	$\partial(u_{a2}^{so}\alpha_{a2}^o/T)/\partial(1/T)$	$\partial b_a/dT$
Na-illite	0.0	0.0	0.0
illite-one	-5.0	-1.0	0.4
illite-two	-5.0	-1.0	0.4
illite-three	-5.0	-1.0	0.4

---

0.604. For illites-5 there is a discontinuous change in  $x_1^s$  from 0.005 to 0.464 at  $x_1^l=0.07$ . Because surface composition is linked to surface area, the discontinuous change in  $x_1^s$  corresponds to a discontinuous change in the state of aggregation.

Fig. 22 shows the results of a phase change on a theoretical isotherm. The abrupt change in the theoretical isotherm of Fig. 22 between points 11 and 12 is due to the predicted transition. The experimental isotherm at point 11 and 12 were determined at  $x_2^l=0.8852$  and  $x_2^l=0.9572$  with model 2 predicting a phase change at  $x_2^l=0.93$ . Fig. 28 shows the drastic decrease in  $x_1^s$  through the phase change, thus producing the unrealistic result in Fig. 22. Fig. 19 for Na-

illite does not show the effects of the phase change because the values of  $x_2^l$  for the first experimental point is greater than the transition value 0.048. Model 2 fits the experimental isotherm significantly better than model 1.

Fits to the experimental heats are shown in Figs. 24 thru 27, where we see that model 2 predicts better over-all fits than model 1. In particular the addition of the "endothermic term"

$$u^s T \left( \frac{\partial \alpha_i}{\partial 1/T} \right)_{P, n_i^s, n_{i+1}^s} \quad (\text{III.21})$$

in equations (II.71) and (II.72), has offset the large exothermic effect (predicted by model one) (see Fig. 15 thru 18) at high  $x_2^l$  values. The peak at low  $x_2^l$  has not been offset as well.

Fig. 24 shows how a phase change affects the heat. Fig. 31 shows a drastic decrease between experimental point 2 at  $x_2^l=0.042$  and experimental point 3 at  $x_2^l=0.0947$ . This is due to the phase change at  $x_2^l=0.048$ . This same effect is seen in fig. 27.

While the predicted phase change is interesting, the data shows no sign of such an effect. Therefore the next step is to choose a form of  $a_s(x_1^s)$  which does not predict a transition.

### Model 3

Model 3 is the same as model 2 except for the form of the specific area. We choose

$$\begin{aligned} a_{sa}(x_{a1}^s, T, P) &= D_a e^{E_a x_{a1}^s + F_a} \\ a_{sb}(x_{b1}^s, T, P) &= D_b e^{E_b x_{b1}^s + F_b} \end{aligned} \quad (\text{III.22})$$

$\alpha_{a1}$ ,  $\alpha_{a2}$ ,  $\alpha_{b1}$ , and  $\alpha_{b2}$  are given by equations (III.8) and (III.9), where

$$\begin{aligned} \left( \frac{\partial a_{sb}}{\partial x_{b1}^s} \right)_{T,P} &= E_b D_b e^{E_b x_{b1}^s + F_b} \\ \left( \frac{\partial a_{sa}}{\partial x_{a1}^s} \right)_{T,P} &= E_a D_a e^{E_a x_{a1}^s + F_a} \end{aligned} \quad (\text{III.23})$$

Table III.6 shows the parameters obtained by fitting the theoretical isotherm to the experimental Na-illite and illite-5 isotherms. Figs. 41 and 42 show  $a_{sa}(x_{a1}^s)$  and  $a_{sb}(x_{b1}^s)$ . No transition is predicted, apparently because these curves are more nearly horizontal than the linear form in the regions  $x_{a1}^s \sim 0$  and  $x_{b2}^s \sim 0$  (where model two predicted transitions).

The heat equations, (III.15), require temperature derivatives of  $a_{sa}$  and  $a_{sb}$ , which are obtained as follows. From equation (III.22)

$$\left( \frac{\partial a_{sa}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} = e^{E_a x_{a1}^s + F_a} \left[ \left( \frac{\partial D_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} + x_{a1}^s D_a \left( \frac{\partial E_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} \right] + \left( \frac{\partial F_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s}$$

As for model 2, we take

Table III.6 Parameters for model 3 isotherms

	$u_{b1}^{so}$	$u_{b2}^{so}$	$u_{a1}^{so}$	$u_{a2}^{so}$		
Na-illite	2.1	-0.95	0.0	0.0		
illite-1	2.1	-0.95	-2.0	0.06		
illite-2	2.1	-0.95	-2.0	0.06		
illite-3	2.1	-0.95	-2.0	0.06		
illite-5	0.0	0.0	-2.0	0.06		
	$D_a$	$E_a$	$F_a$	$D_b$	$E_b$	$F_b$
Na-illite	0.0	0.0	0.0	150	-4.0	115
illite-1	2.7	3.9	130	150	-4.0	115
illite-2	2.7	3.9	130	150	-4.0	115
illite-3	2.7	3.9	130	150	-4.0	115
illite-5	2.7	3.9	130	0.0	0.0	0.0

$$\left( \frac{\partial a_{sa}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} = 0 \quad @ \quad x_{a1}^s = 1 \quad (\text{III.25})$$

thus equation (III.24) becomes

$$\begin{aligned} \left( \frac{\partial a_{sa}}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} = & e^{E_a x_{a1}^s} \left[ \left( \frac{\partial D_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} + x_{a1}^s D_a \left( \frac{\partial E_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} \right] \\ & - e^{E_a} \left[ \left( \frac{\partial D_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} + D_a \left( \frac{\partial E_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} \right] \end{aligned} \quad (\text{III.26})$$

From equation (III.23)

$$\frac{\partial}{\partial T} \left[ \left( \frac{\partial a_{sa}}{\partial x_{a1}^s} \right)_{T,P} \right]_{P, n_{a1}^s, n_{a2}^s} \\ = e^{E_a x_{a1}^s} \left[ D_a \left( \frac{\partial E_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} + E_a \left( \frac{\partial D_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} + x_{a1}^s D_a E_a \left( \frac{\partial E_a}{\partial T} \right)_{P, n_{a1}^s, n_{a2}^s} \right]$$

(III.27)

From equation (III.22)

$$\left( \frac{\partial a_{sb}}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} = e^{E_b x_{b1}^s} \left[ \left( \frac{\partial D_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} + x_{b1}^s D_b \left( \frac{\partial E_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} \right] + \left( \frac{\partial F_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s}$$

As for model 2, we take

(III.28)

$$\left( \frac{\partial a_{sb}}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} = 0 \quad @ \quad x_{b1}^s = 0 \quad (III.29)$$

equation (III.28) becomes

$$\left( \frac{\partial a_{sb}}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} = e^{E_b x_{b1}^s} \left[ \left( \frac{\partial D_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} + x_{b1}^s D_b \left( \frac{\partial E_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} \right] - \left( \frac{\partial D_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s}$$

(III.30)

From equation (III.23)

$$\frac{\partial}{\partial T} \left[ \left( \frac{\partial a_{sb}}{\partial x_{b1}^s} \right)_{T,P} \right]_{P, n_{b1}^s, n_{b2}^s} \\ = e^{E_b x_{b1}^s} \left[ D_b \left( \frac{\partial E_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} + E_b \left( \frac{\partial D_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} + x_{b1}^s D_b E_b \left( \frac{\partial E_b}{\partial T} \right)_{P, n_{b1}^s, n_{b2}^s} \right] \quad (III.31)$$

Direct substitution of equations (III.26), (III.27), (III.30),



Table III.7

Parameters for model 3 heats

	$\partial(u_{b1}^{so}\alpha_{b1}^o/T)/\partial(1/T)$	$\partial(u_{b2}^{so}\alpha_{b2}^o/T)/\partial(1/T)$		
Na-illite	-23.0	-3.0		
illite-one	-23.0	-3.0		
illite-two	-23.0	-3.0		
illite-three	-23.0	-3.0		
	$\partial(u_{a1}^{so}\alpha_{a1}^o/T)/\partial(1/T)$	$\partial(u_{a2}^{so}\alpha_{a2}^o/T)/\partial(1/T)$		
Na-illite	0	0		
illite-one	-3.8	-2.5		
illite-two	-3.8	-2.5		
illite-three	-3.8	-2.5		
	$(\partial D_a/\partial T)$	$(\partial E_a/\partial T)$	$(\partial D_b/\partial T)$	$(\partial E_b/\partial T)$
Na-illite	0	0	0.2	-0.3
illite-one	-0.085	0.026	0.2	-0.3
illite-two	-0.085	0.026	0.2	-0.3
illite-three	-0.085	0.026	0.2	-0.3

and (III.31) into equations (III.15), gives the temperature derivatives of  $\alpha_{a1}$ ,  $\alpha_{a2}$ ,  $\alpha_{b1}$ , and  $\alpha_{b2}$ . Table III.7 shows the parameters obtained by fitting the theoretical heats to the experimental heats Na-illite and illite-3.

### Discussion of Model 3

Fits to the experimental isotherms are shown in Figs. 32 thru 36, where we see essentially the same fit as predicted by model 2.

Fits to the experimental heats are shown in Figs. 37 thru 40, where we see a much improved fit than predicted by model 2. With the addition (as compared to model 2) of two variational parameters, the large exothermic effect at small  $x_2^l$  values (as seen in Figs. 24 thru 27) has been eliminated.

### IV Results for Montmorillonite

#### Model 4

Model 4 is exactly the same as model 2, with the exception of the adsorbent. In model 4 the montmorillonite is the adsorbent. Table IV.1 shows parameters used in model 4. Table IV.2 shows the parameters obtained by fitting the theoretical isotherm to the experimental Na-montmorillonite and montmorillonite-6. Table IV.3 shows the parameters obtained by fitting the theoretical heats to the experimental heats of Na-montmorillonite and montmorillonite-2. Figs. 52 and 53 show  $a_{sa}(x_{a1}^s)$  and  $a_{sb}(x_{b1}^s)$ . No phase transition is predicted in model 4.

Table IV.1      Parameters used in model 4

$\tau_{12}=3.104$		$Z_a$	$Z_b$
$\tau_{21}=0.243$	Na-mont	0	1
$V_1^l=90.5\text{cm}^3/\text{mole}$	mont-1	0.22	0.78
$V_2^l=41.1\text{cm}^3/\text{mole}$	mont-2	0.44	0.56
$a_1=180\text{m}^2/\text{mmole}$	mont-3	0.62	0.38
$a_2=95\text{m}^2/\text{mmole}$	mont-4	0.76	0.24
$\tau_{12}'=1.5$	mont-5	0.9	0.1
$\tau_{21}'=1.1$	mont-6	1.0	0.0

Table IV.2            parameters for model 4 isotherms

	$u_{b1}^{so}$	$u_{b2}^{so}$	$u_{a1}^{so}$	$u_{a2}^{so}$
Na-mont	1.6	-14.0	0.0	0.0
mont-1	1.6	-14.0	2.2	0.4
mont-2	1.6	-14.0	2.2	0.4
mont-3	1.6	-14.0	2.2	0.4
mont-4	1.6	-14.0	2.2	0.4
mont-5	1.6	-14.0	2.2	0.4
mont-6	0.0	0.0	2.2	0.4

	$b_b$	$M_b$	$b_a$	$M_a$
Na-mont	365	-162	0	0
mont-1	365	-162	45	1000
mont-2	365	-162	45	1000
mont-3	365	-162	45	1000
mont-4	365	-162	45	1000
mont-5	365	-162	45	1000
mont-6	0	0	45	1000

---

Table IV.3      parameters for model 4 heats

	$\partial(u_{b1}^{so}\alpha_{b1}^o/T)\partial(1/T)$	$\partial(u_{b2}^{so}\alpha_{b2}^o/T)\partial(1/T)$
Na-mont	17.0	-19.0
mont-2	17.0	-19.0

	$\partial(u_{a1}^{so}\alpha_{a1}^o/T)\partial(1/T)$	$\partial(u_{a2}^{so}\alpha_{a2}^o/T)\partial(1/T)$
Na-mont	0.0	0.0
mont-2	-5.0	18.0

	$(\partial M_b/\partial T)$	$(\partial b_a/\partial T)$
Na-mont	12.0	0
mont-2	12.0	-8.0

---

Fits to the experimental isotherms are shown in Figs. 43 thru 49, where we see an excellent overall fit. Fits to the experimental heats of Na-montmorillonite and montmorillonite-2 (other experimental heats were not available) are shown in Figs. 50 and 51, where we see a good fit with a slight overabundant exothermic effect at small  $x_2^I$  values.

## V. Swelling and disaggregation in Montmorillonites and Illites

In section V we look at how our theory predicts the heat effect due to swelling for montmorillonites and disaggregation for illites. In particular we are interested in the contribution from equation (III.21), the term responsible for the heat of immersion due to swelling or disaggregation.

### Montmorillonites

Using the results from model 4 figs. 54 and 55 show the individual contributions of the heat of immersion for Na-mont and Mont-2. Both Na-mont and Mont-2 have similar swelling contributions throughout the concentration range with the exception of Mont-2 where our theory predicts a large endothermic effect due to the swelling term between  $x_2^l=0.85$  and  $x_2^l=1.0$  which is due to the enrichment of benzene in solution. Figs. 56 and 57 show the individual contributions of the heat of immersion for the non-polar(surface A) and the polar(surface B) "patches" of Mont-2. Fig. 56 indicates that at the polar surface the swelling term is responsible for the slight endothermic effect at low  $x_2^l$  values. Fig. 57 indicates that at the non-polar surface the surface term is largely responsible for the endothermic effect with a small endothermic contribution from the swelling term at high  $x_2^l$

values.

In general for Na-mont our theory predicts some swelling with the enrichment of methanol. For Mont-2 our theory predicts swelling with the enrichment of methanol due to the polar surface and swelling with the enrichment of benzene due to the non-polar surface. The endothermic contribution due to the non-polar surface term is interesting and suggests that there is a fundamental difference between the stickiness of the non-polar and polar surfaces.

### Illites

Using the results from model 3 figs 58 and 59 show the individual contributions of the heat of immersion for Na-illite and illite-3 respectively. Fig. 58 shows our theory predicts Na-illite as having an endothermic contribution from the disaggregation term at small  $x_2^l$  values and an exothermic contribution throughout the rest of the concentration range for illite 3. Fig. 59 shows an endothermic contribution from the disaggregation term throughout the concentration range. Figs 60 and 61 show the individual contributions of the heat of immersion for the non-polar(surface A) and the polar(surface B) "patches" of illite-3. Fig 60 indicates that at the polar surface the disaggregation term is responsible for the endothermic effect at small  $x_2^l$  values and the exothermic effect throughout the rest of the concentration

range for illite-3. Fig 61 indicates that at the non-polar surface the disaggregation term is responsible for the endothermic effect throughout the concentration range.

In general for Na-illite our theory indicates disaggregation at small  $x_2^l$  values due to the enrichment of methanol in the bulk liquid. At larger values of  $x_2^l$  we see with the enrichment of benzene, Na-illite tends to aggregate, thus the exothermic heat contribution. In the case of illite-3, as expected the polar surface behaves like Na-illite. The non-polar surface of illite-3 shows disaggregation at large values of  $x_2^l$  due to the enrichment of benzene. At smaller values of  $x_2^l$  we see a decrease in disaggregation of the non-polar surface.

## VII Conclusions

In this section we compare results from our self-consistent thermodynamic model to Dekany et al's ad hoc model.

The first comparison is the adsorption capacities. The adsorption capacities are determined for pure components one and two. Dekany defines the monomolecular adsorption capacity of pure component one as



$$n_{1,o}^s = \frac{a_{equ}^s}{a_1} = n_1^s + \beta n_2^s \quad (\text{VII.2})$$

and similarly for pure component two. We compare are adsorption capacities with Dekany's under similar conditions. In our calculation of adsorption capacities for pure components one and two we use

$$n_{1,o}^s = \frac{a_s}{a_2} = \frac{a_{sb} \bar{m}_b Z_b + a_{sa} \bar{m}_a Z_a}{\bar{m} a_1} \quad (\text{VII.3})$$

$$n_{2,o}^s = \frac{a_s}{a_2} = \frac{a_{sb} \bar{m}_b Z_b + a_{sa} \bar{m}_a Z_a}{\bar{m} a_2}$$

where  $a_{sb}(x_{b1}^s)$ , and  $a_{sa}(x_{a1}^s)$  are evaluated at

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Table VII.1 Adsorption capacities for illites

	Dekany	
	$n_{2,o}^s$	$n_{1,o}^s$
	(mmole/g)	
Na-illite	1.06	0.56
illite-1	1.84	0.97
illite-2	1.89	1.00
illite-3	1.85	0.93
illite-5	1.81	0.96

---

the point in which our isotherm has it's least curvature. We see from tables (VII.1), (VII.2), and (VII.3), that our

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Table VII.2 Adsorption capacities for montmorillinites

	Dekany	
	$n_{2,0}^s$	$n_{1,0}^s$
	(mmole/g)	
Na-mont	3.40	1.79
mont-1	4.72	2.49
mont-2	5.69	3.01
mont-3	6.69	3.53
mont-4	7.72	4.07
mont-5	8.04	4.24
mont-6	8.19	4.32

---

adsorption capacities for both adsorbents are in good agreement with Dekany's.

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Table VII.3 Our altered adsorption capacities

	$n_{2,0}^s$	$n_{1,0}^s$
	(mmole/g)	
Na-mont	3.79	2.00
mont-1	4.69	2.47
mont-2	5.47	2.87
mont-3	6.07	3.20
mont-4	6.50	3.43
mont-5	7.02	3.71
mont-6	7.28	3.84
Na-illite	2.00	1.05
illite-1	1.96	1.01
illite-2	1.97	1.04
illite-3	1.98	1.04
illite-5	1.97	1.04

---

Next we consider the heats of immersion. Our interpretation of the heat of adsorption is similar in some respects to Dekany's. The basis of Dekany's analysis is the 'two segment' model described on page 14; he pictures the heat as arising from a two-segment ideal term plus corrections. Dekany's "ideal" contributions correspond closely to our "surface" contributions, which are plotted in Figs. 62 thru 67. We do see contributions like Dekany's 'double segments' in Figs. 62, 63, and 66. Fig. 64 has a single segment because only the polar surface is present. Fig. 65 and 67 are examples where the surface terms do not cleanly resolve into two straight segments due primarily to swelling and/ or disaggregation. In summary, both we and Dekany picture the heat as due to a "surface" (or "ideal") term plus corrections, but our surface terms do not always exhibit the two-segment behavior that Dekany assumes.

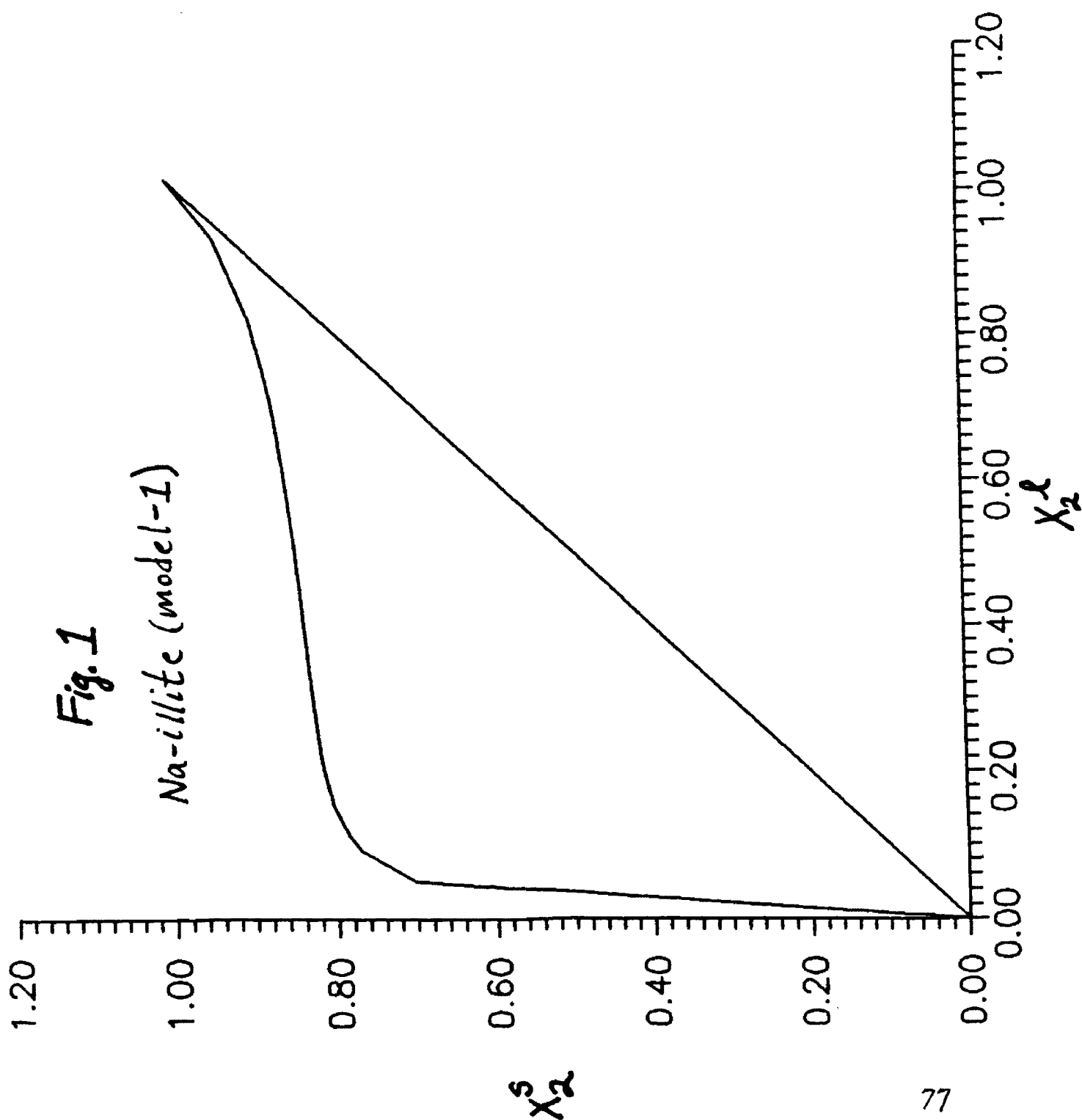
In conclusion, even though our calculation of the adsorption isotherms are fundamentally different than Dekany's adsorption isotherms, the picture of methanol preferentially adsorbing to the polar surface, and the benzene preferentially adsorbing to the non-polar surface, is evident from both Dekany's and our isotherm calculations. Our analysis of the heat of immersion differs from Dekany's primarily in the correction terms. Dekany omits contributions from the bulk heats, but we include them because they are well-characterized from studies of bulk liquids and their size is significant.

Studies based on our model 1 have demonstrated that bulk corrections are not enough: an additional endothermic correction is required to compensate for the large exothermic bulk corrections seen in Figs. 11-14. Reasonable extra corrections are the non-ideality of the surface and disaggregation or swelling. We chose to model disaggregation and/ or swelling because it is known to occur in some of the studied systems and because it offers an endothermic contribution in the concentration ranges where surface structures are changing. It seems unlikely that the heat from surface non-ideality will compensate for the bulk non-ideality because surface and bulk compositions are generally very different. After including surface, bulk, and disaggregation/swelling corrections in our model, we found satisfactory agreement with experiment. By contrast, Dekany arbitrarily assigns virtually all the corrections to surface non-ideality.

Elementary treatments of adsorption heats usually include no corrections to what we call the "surface" effect and very often give satisfactory fits to data. Our studies suggest why: other effects are present--most confidently the "bulk" corrections--but they tend to compensate for one another.

Fig. 1

Na-illite (model-1)



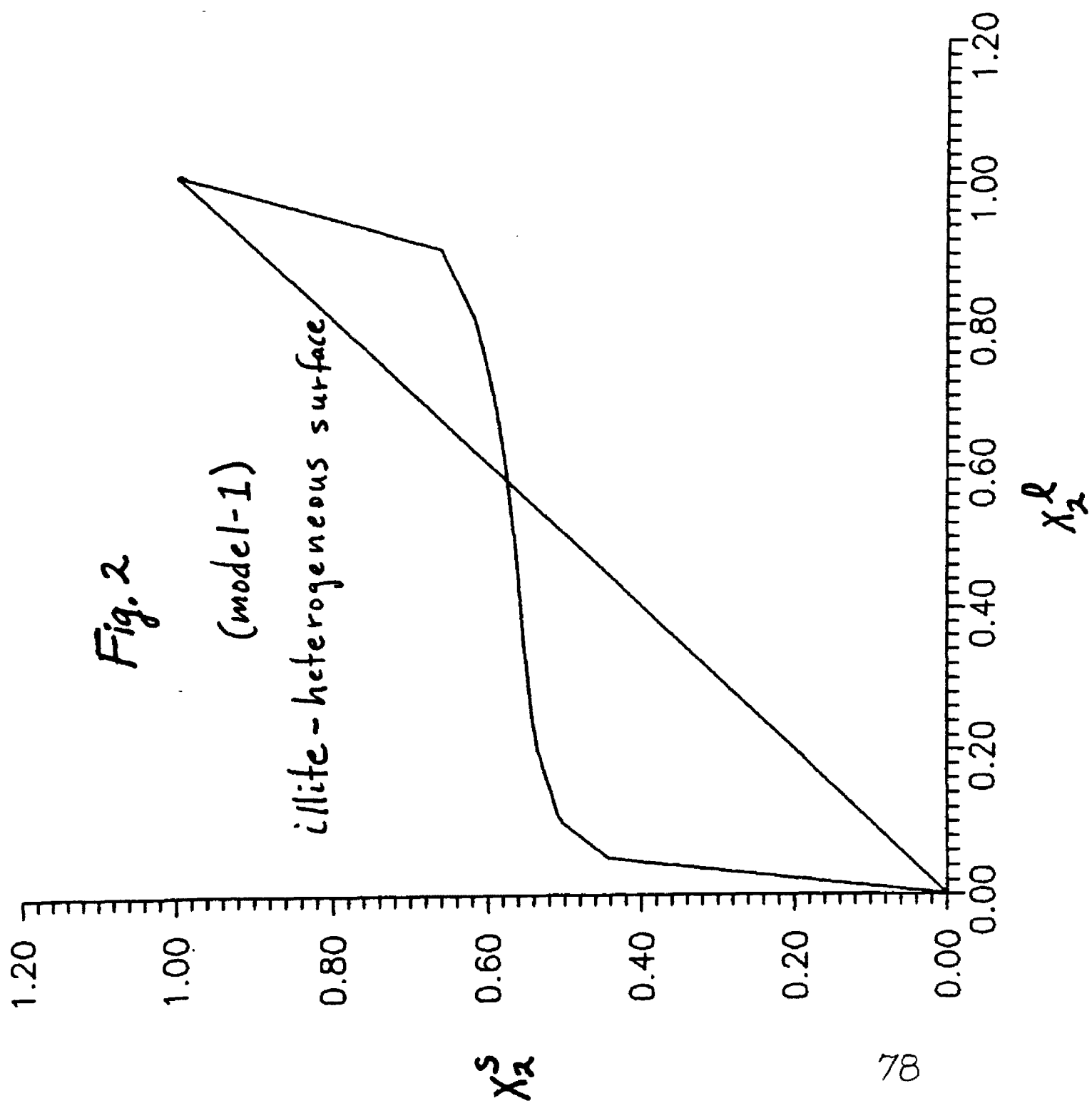
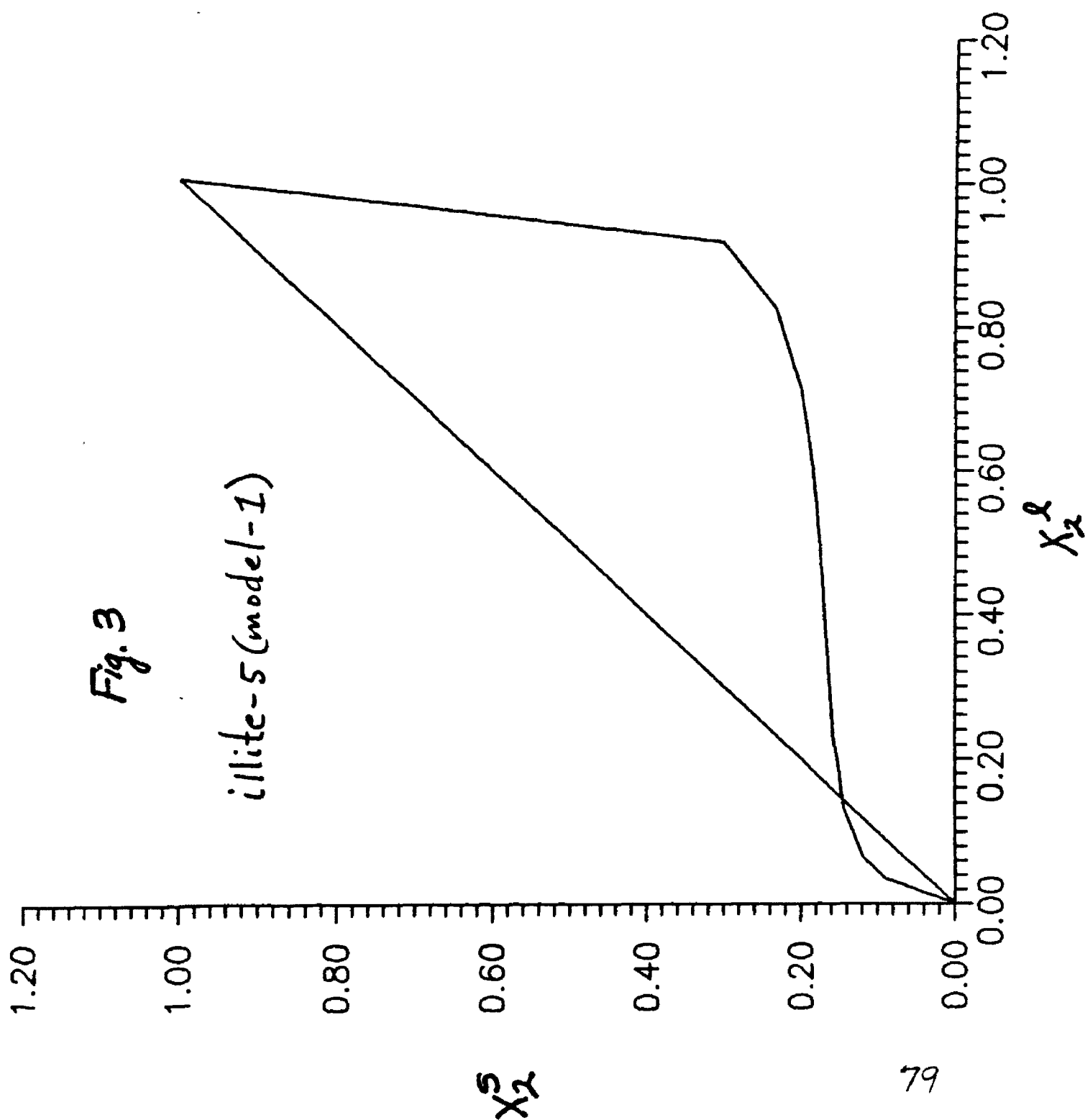
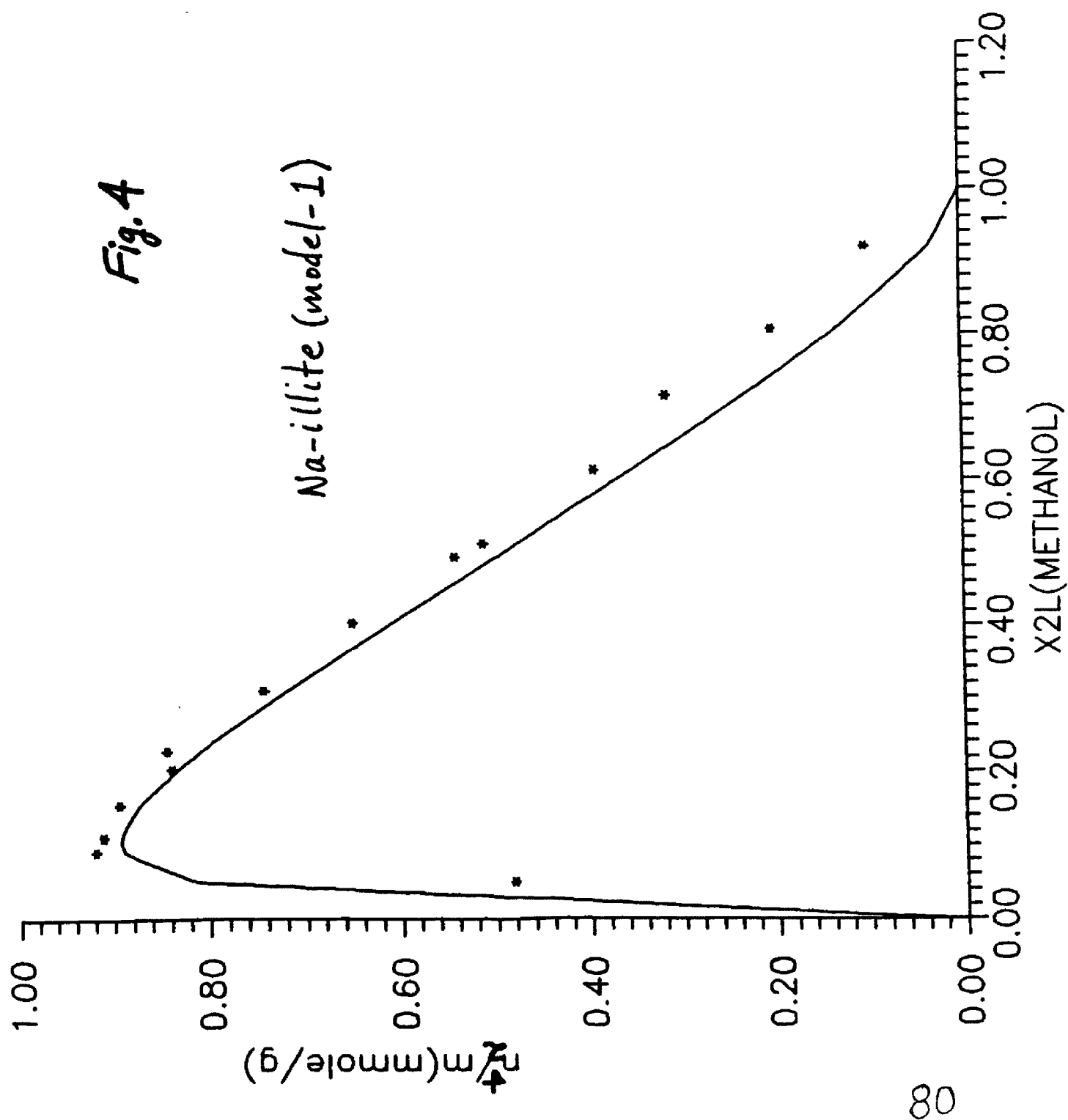


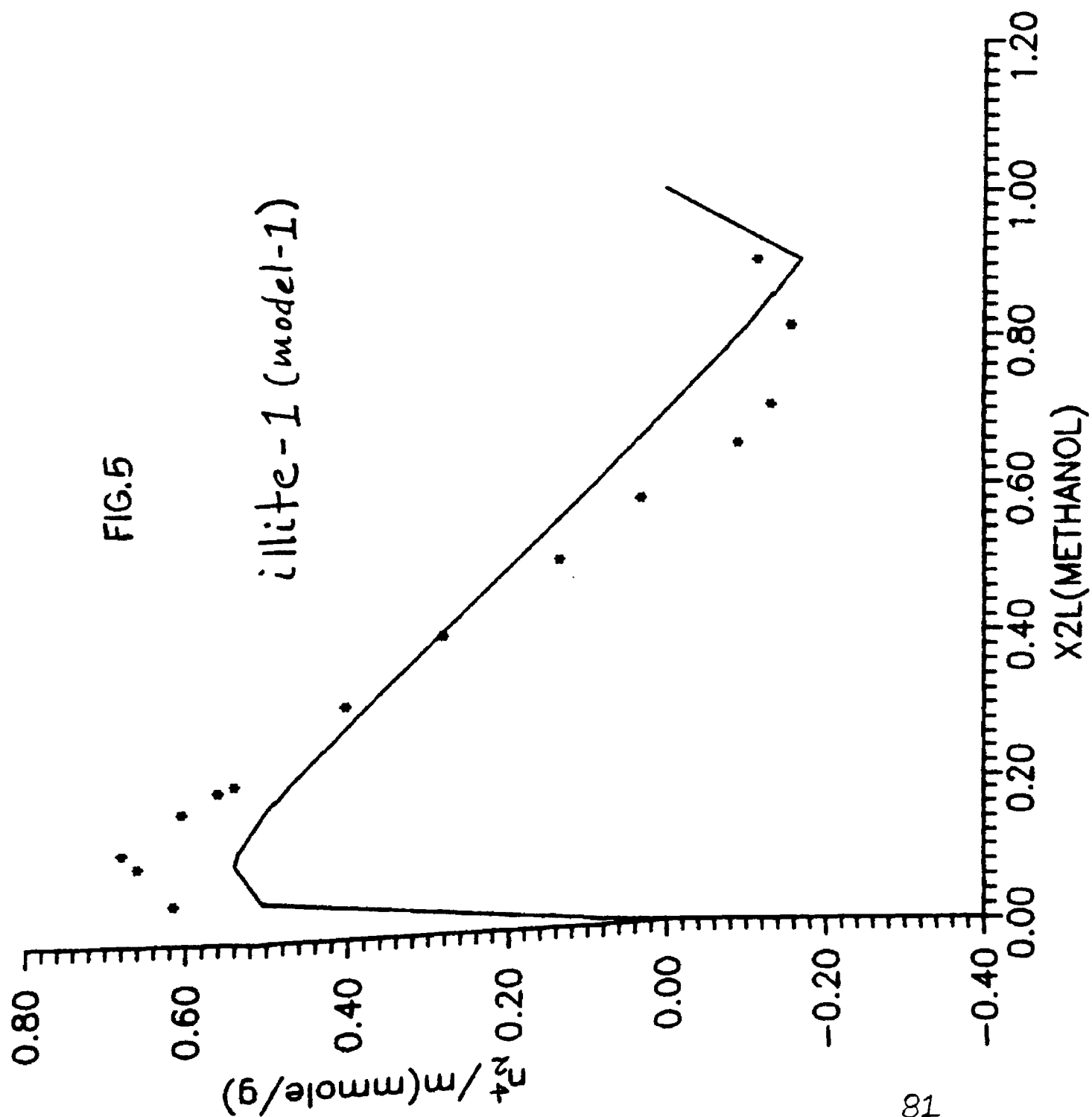
Fig. 3

illite-5 (model-1)









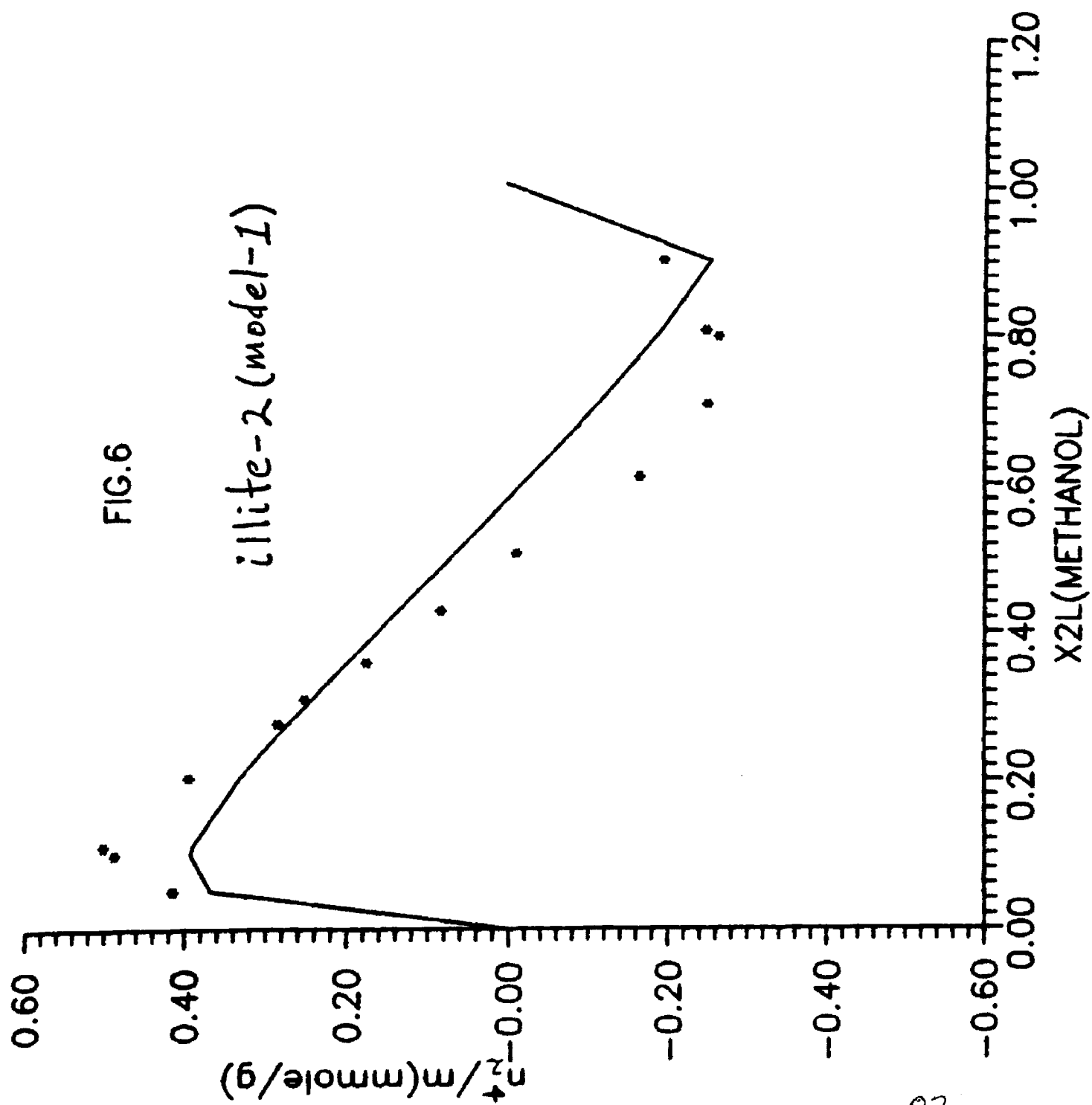
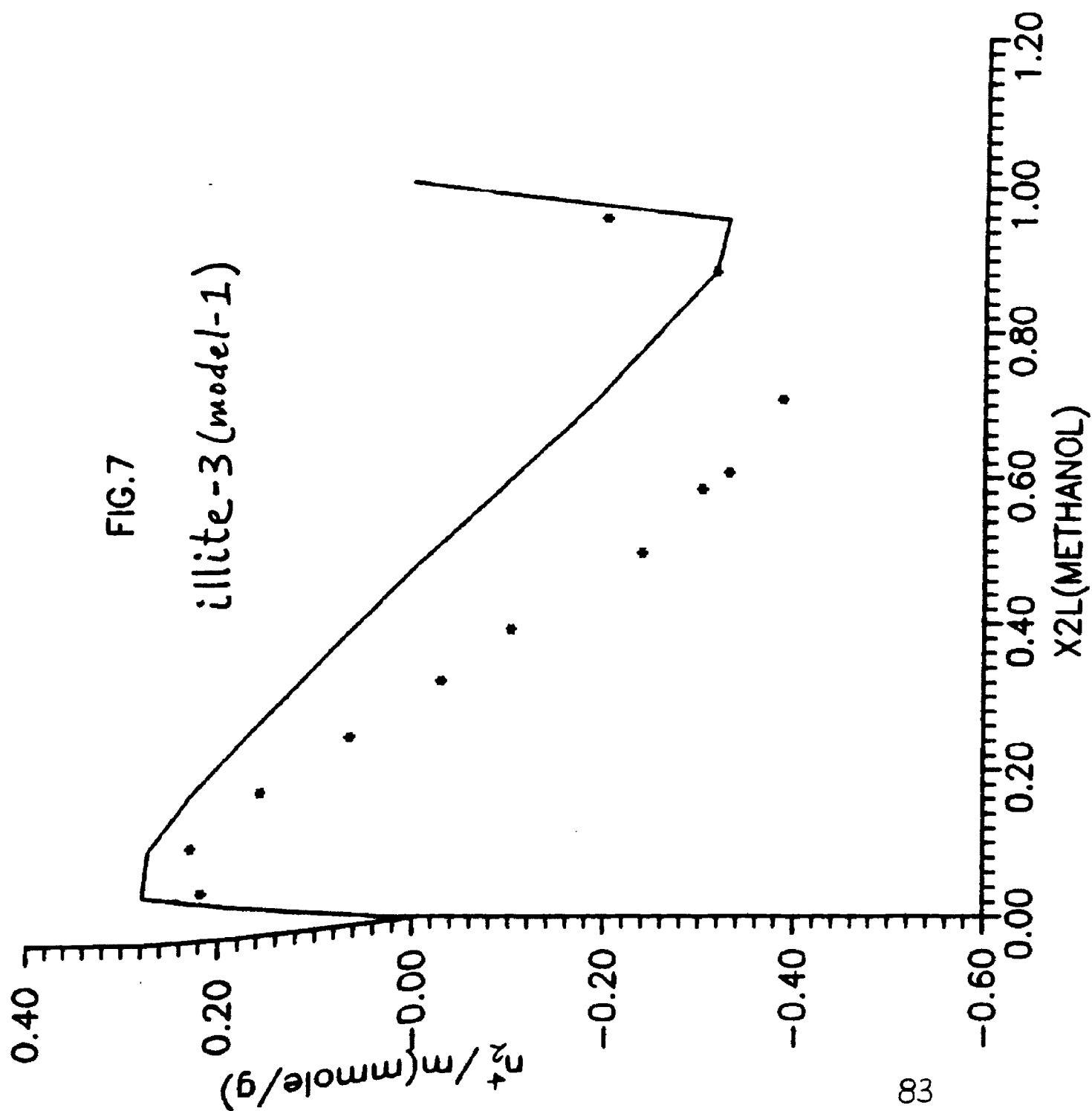


FIG.7

illite-3(model-1)



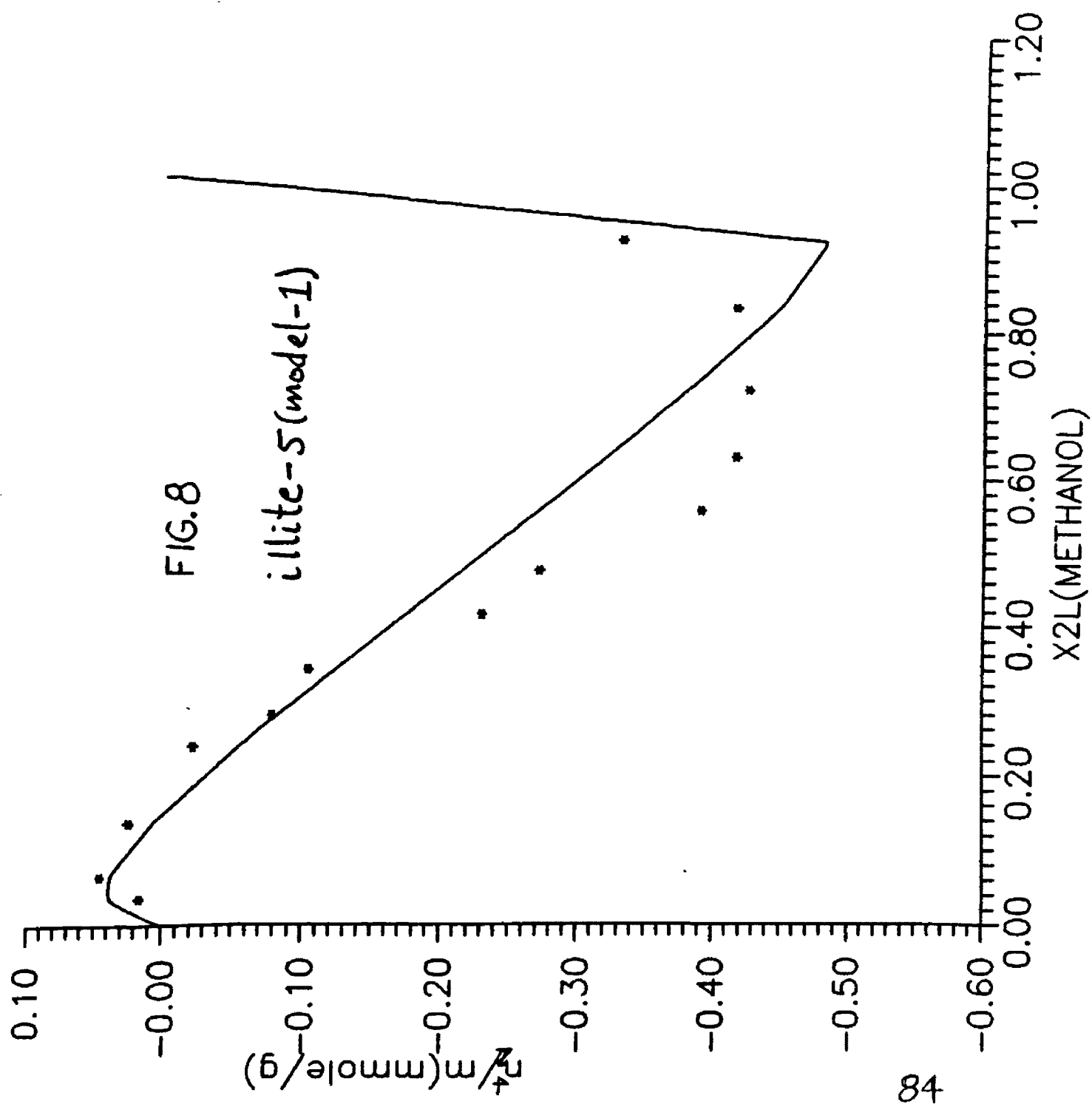
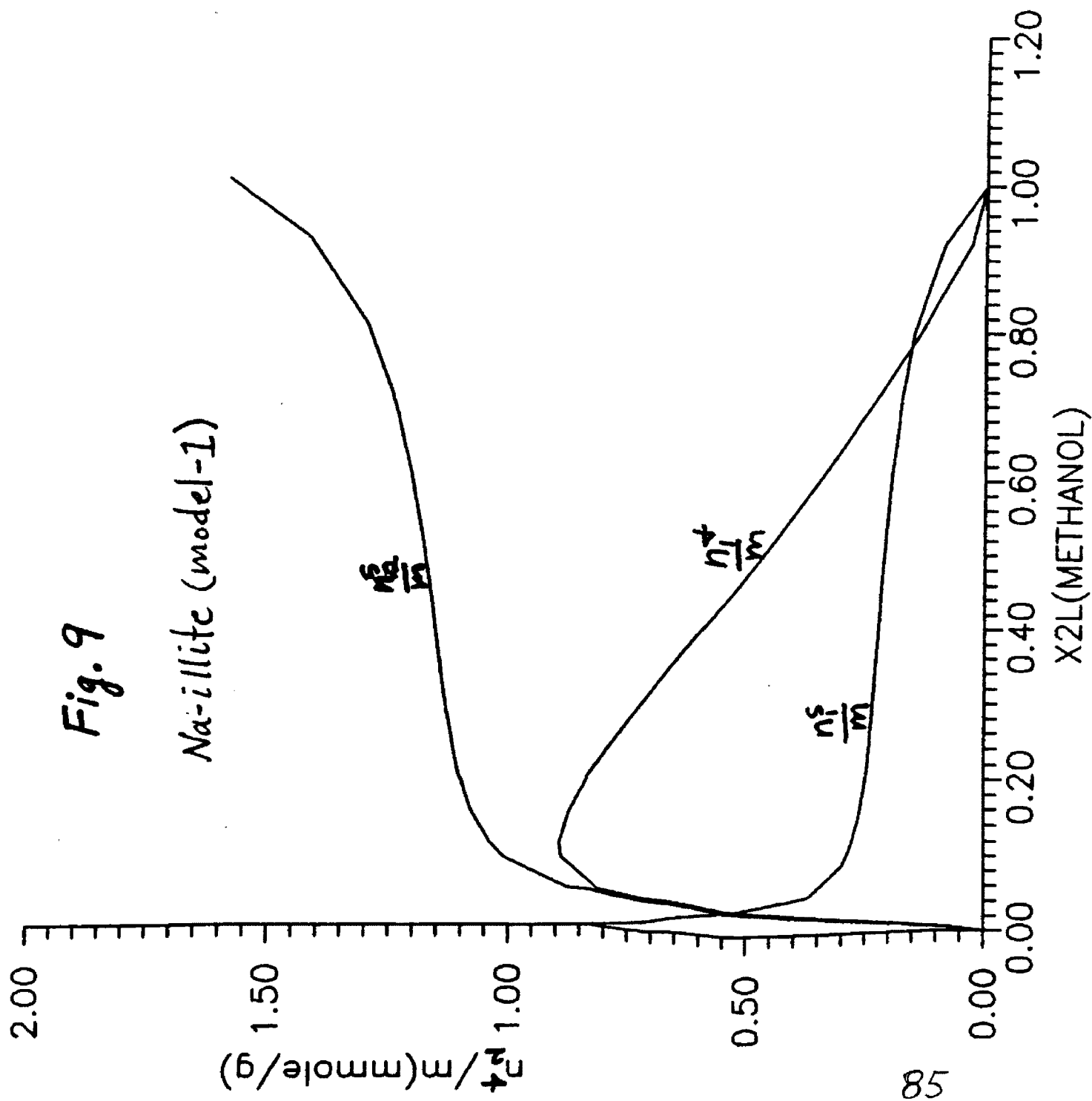
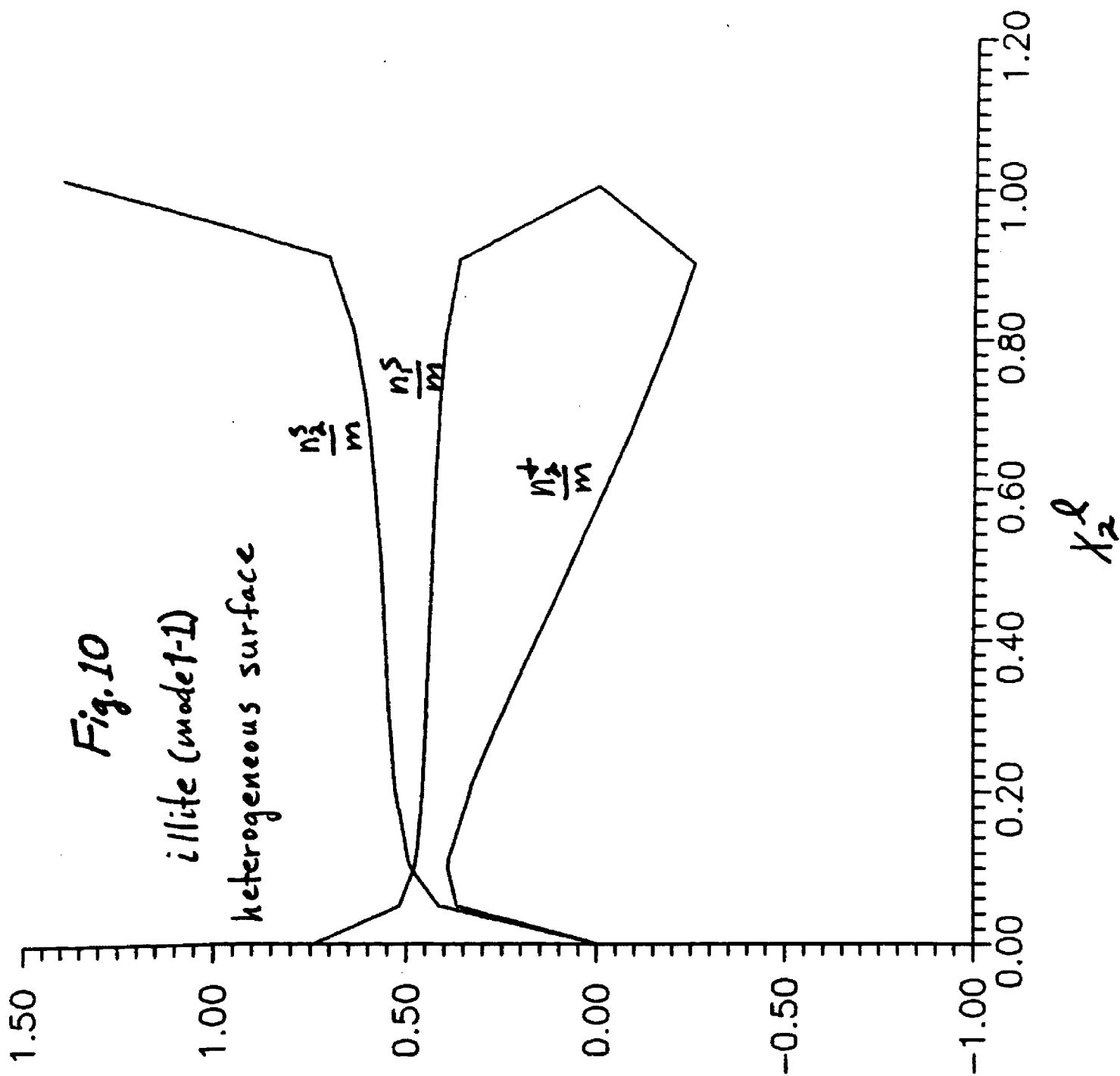


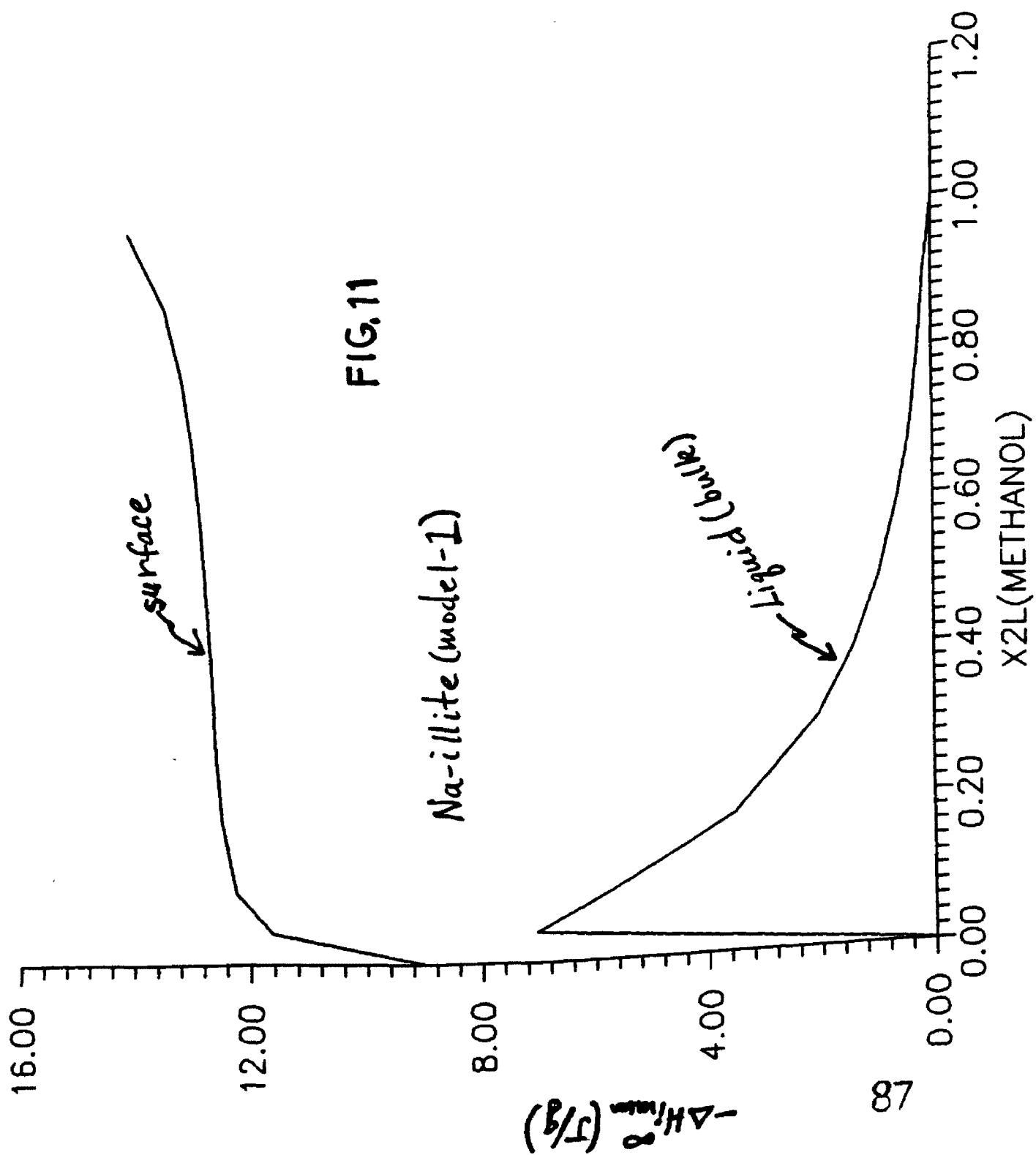
Fig. 9

Na-illite (model-1)

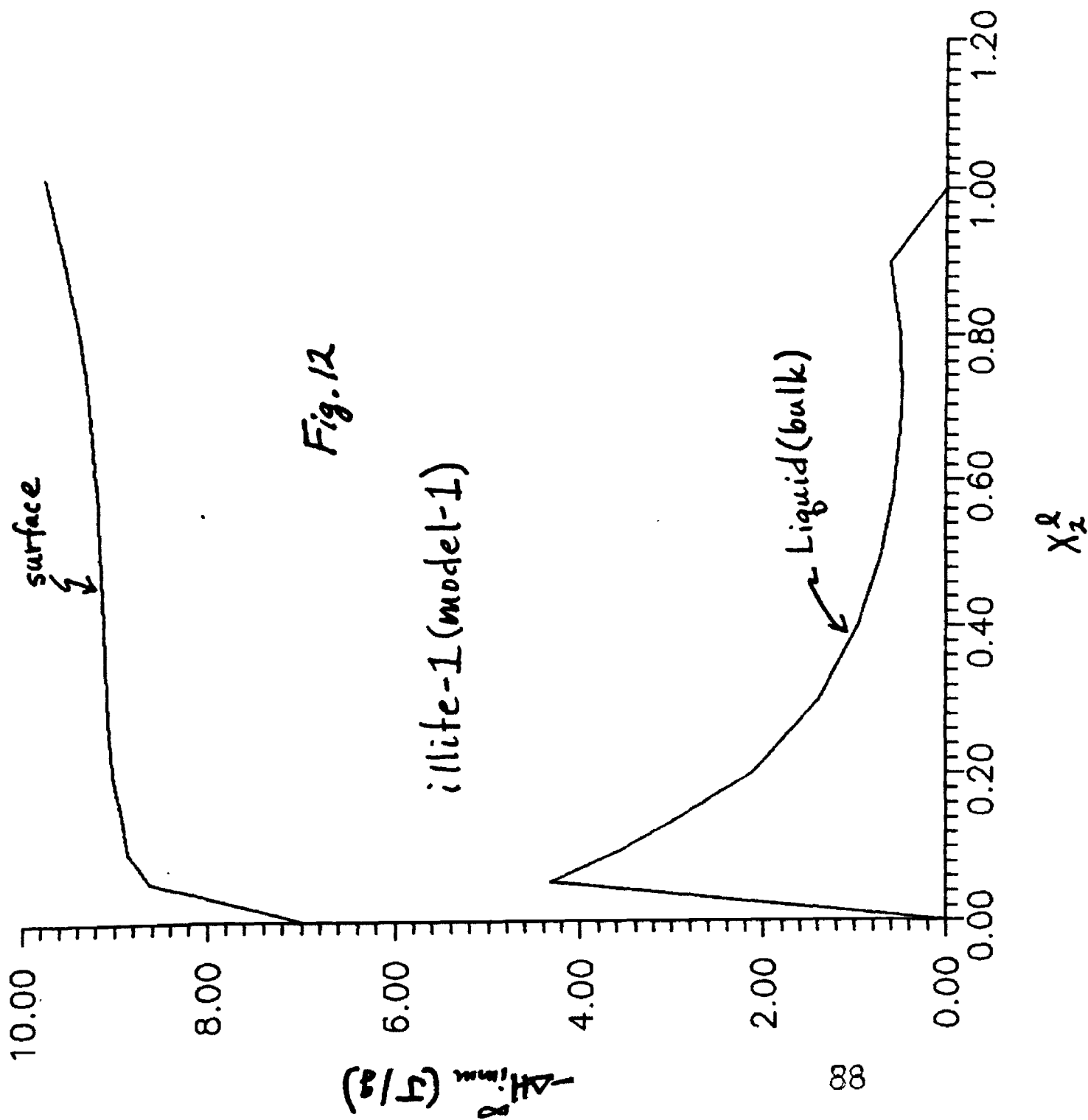


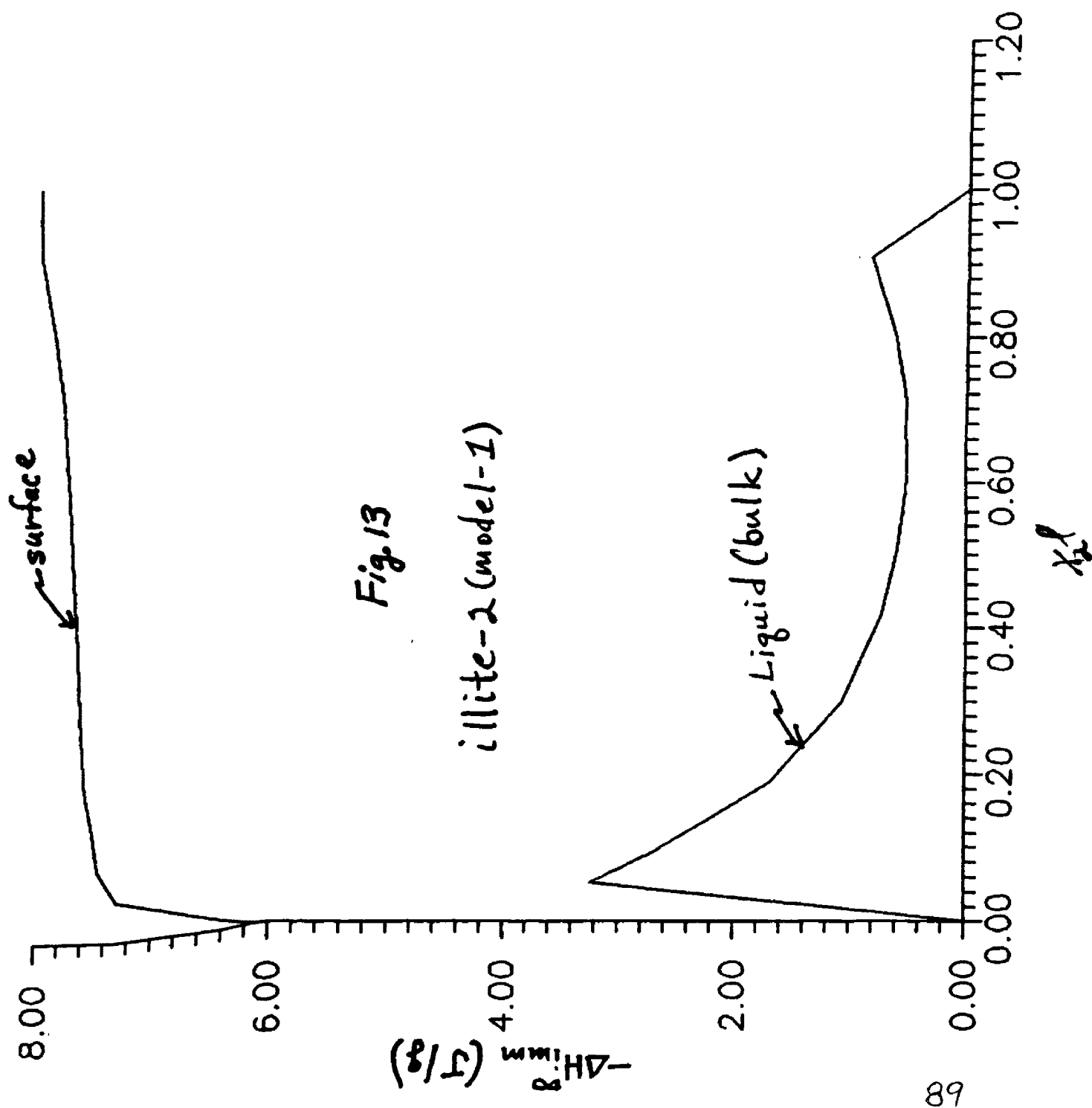
85



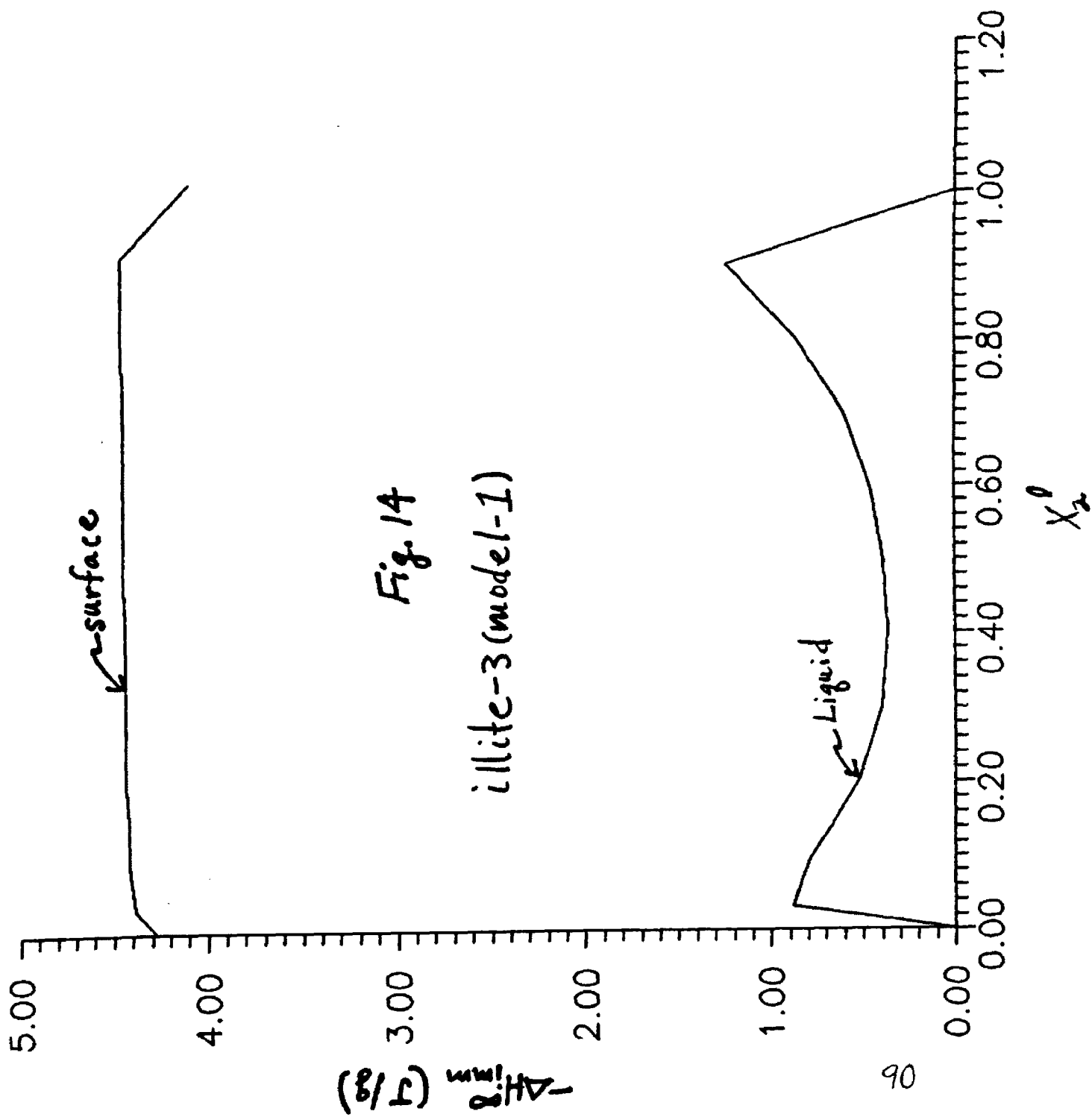


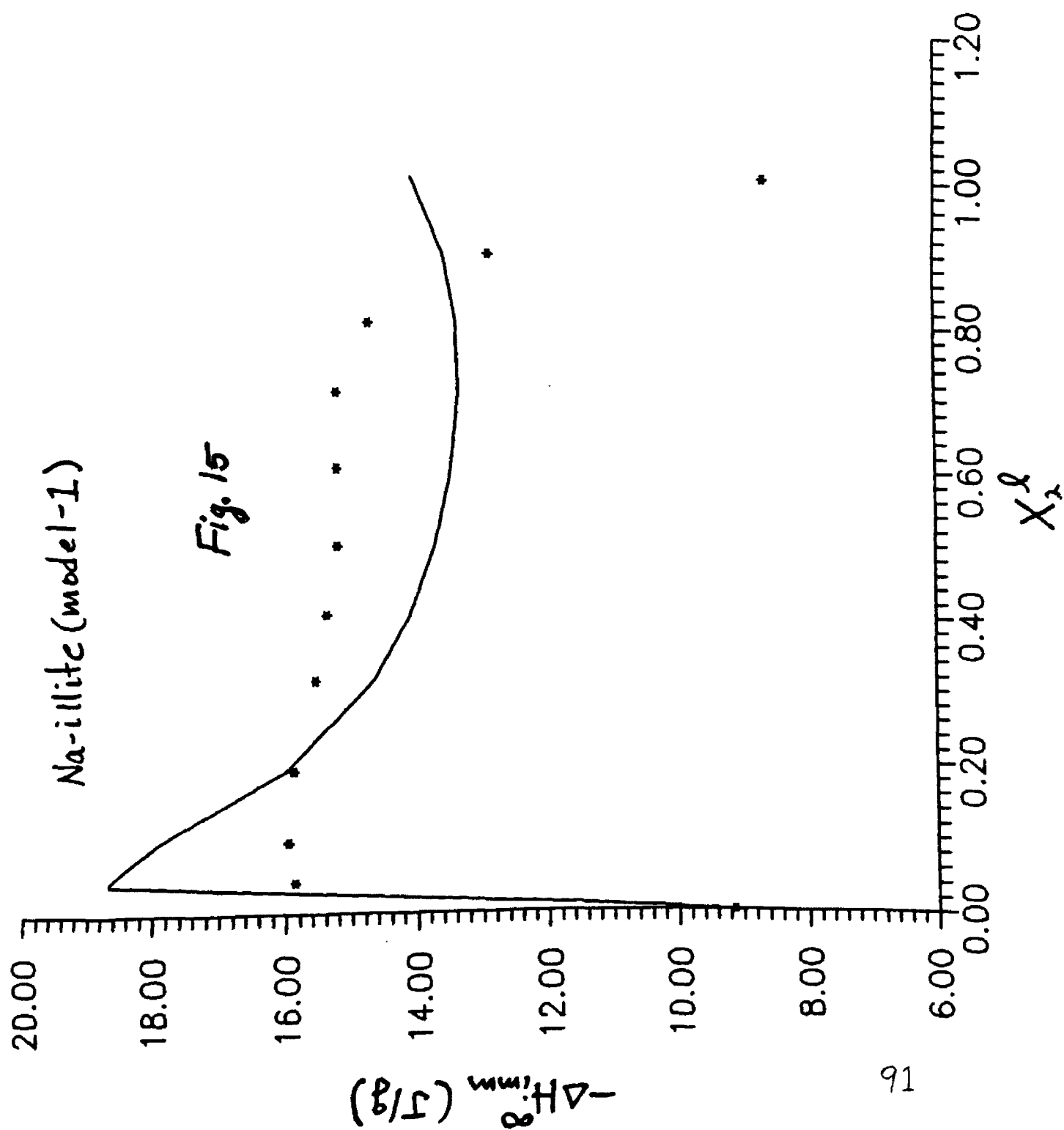


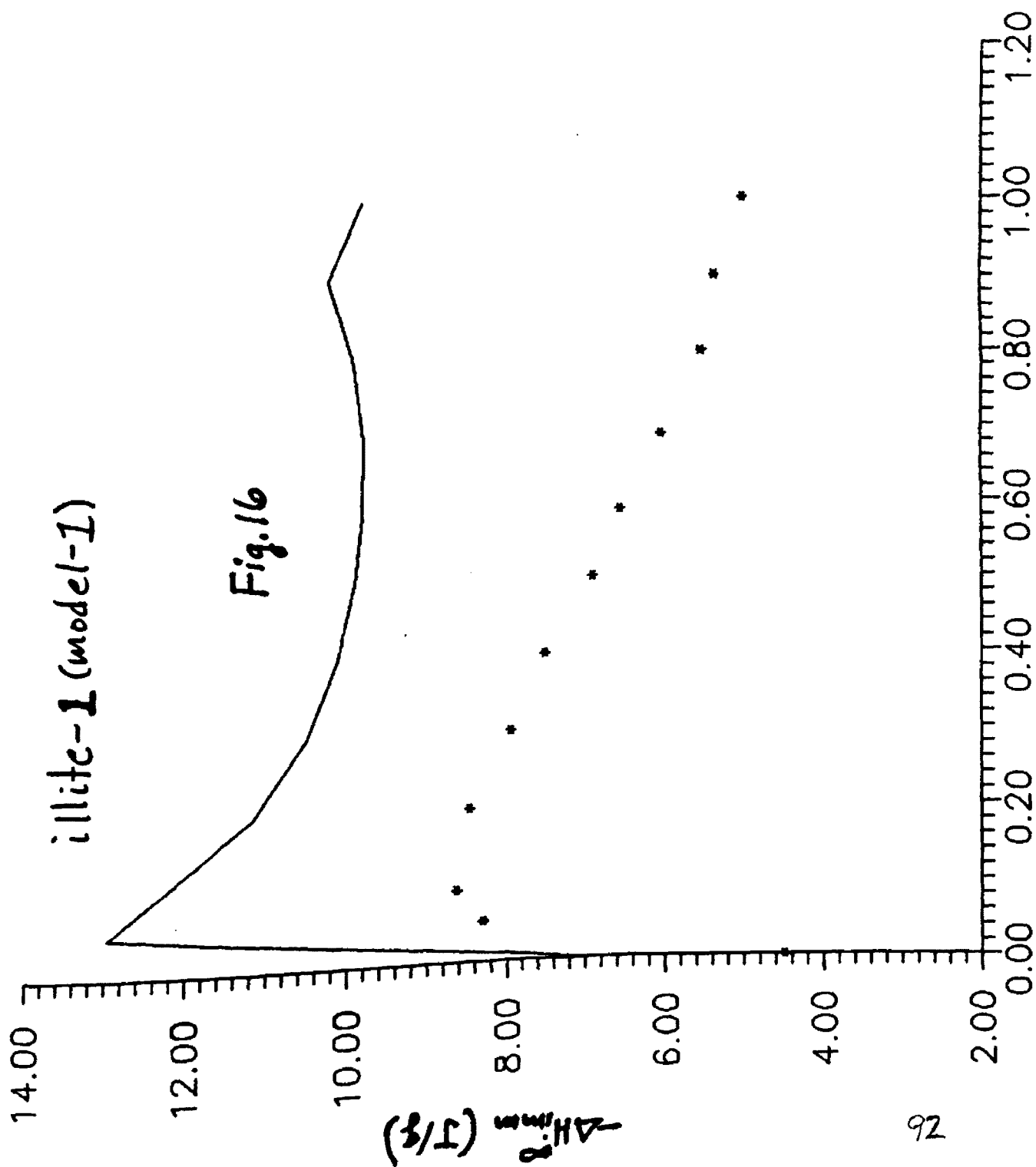


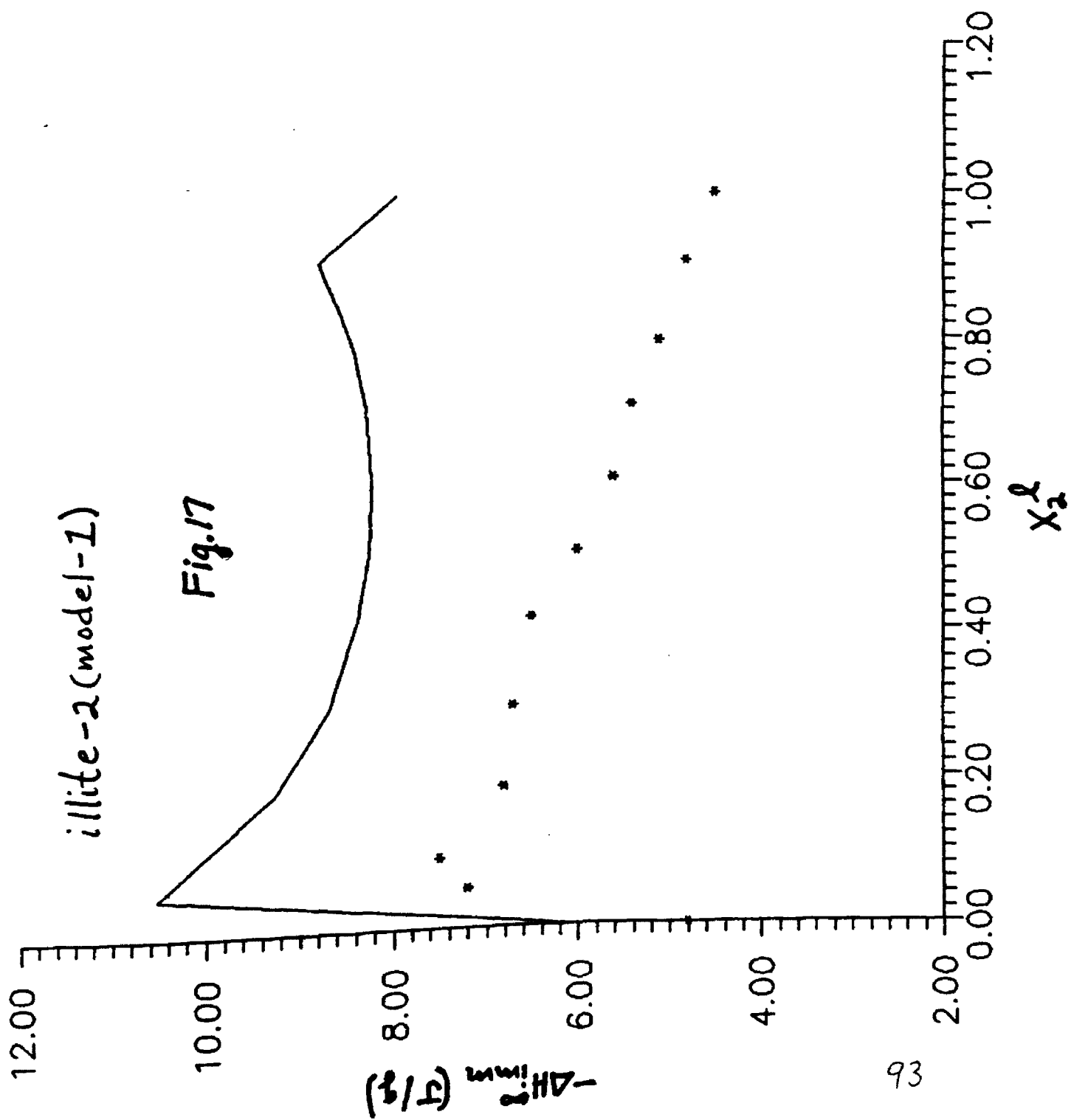


89

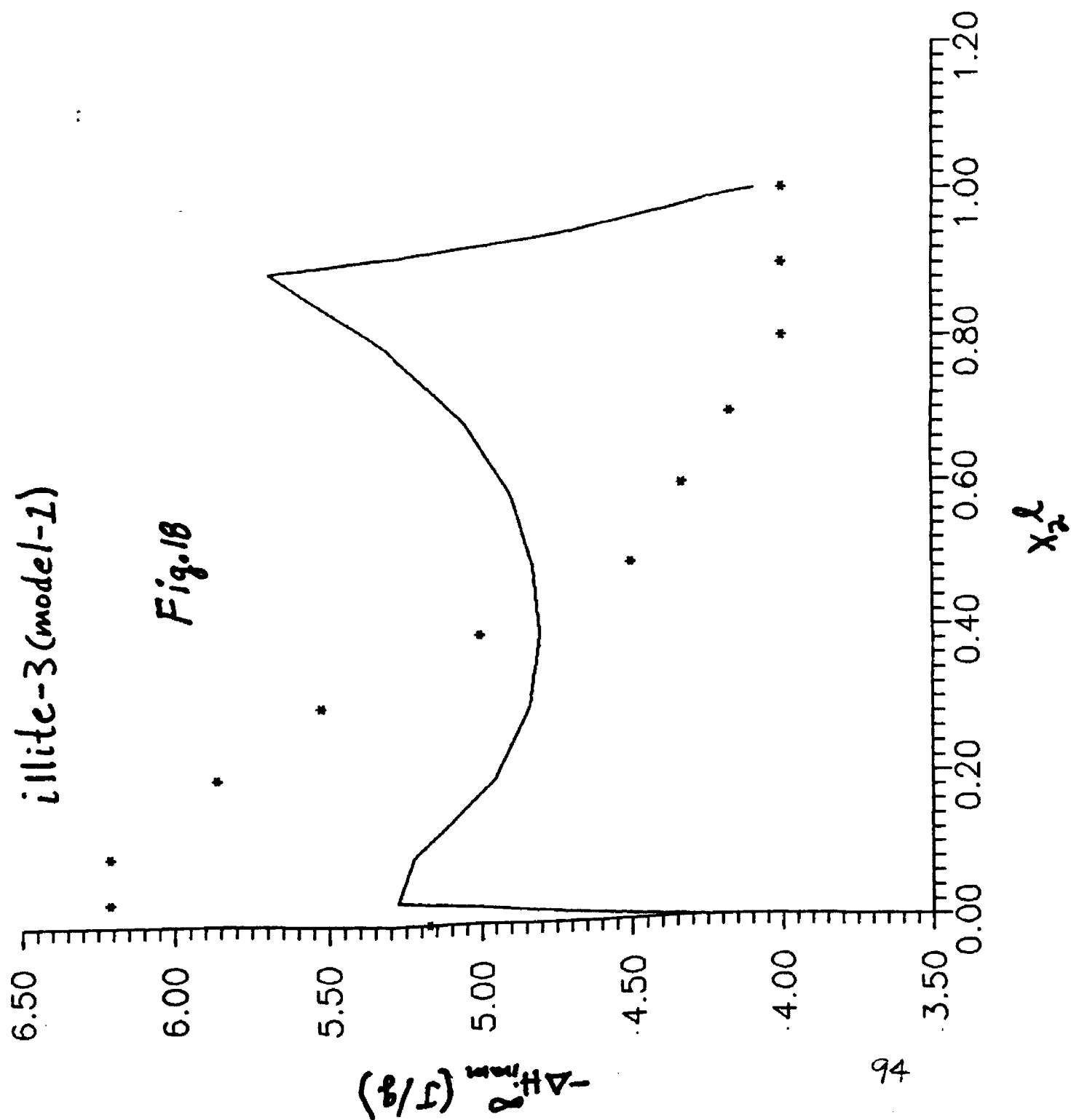


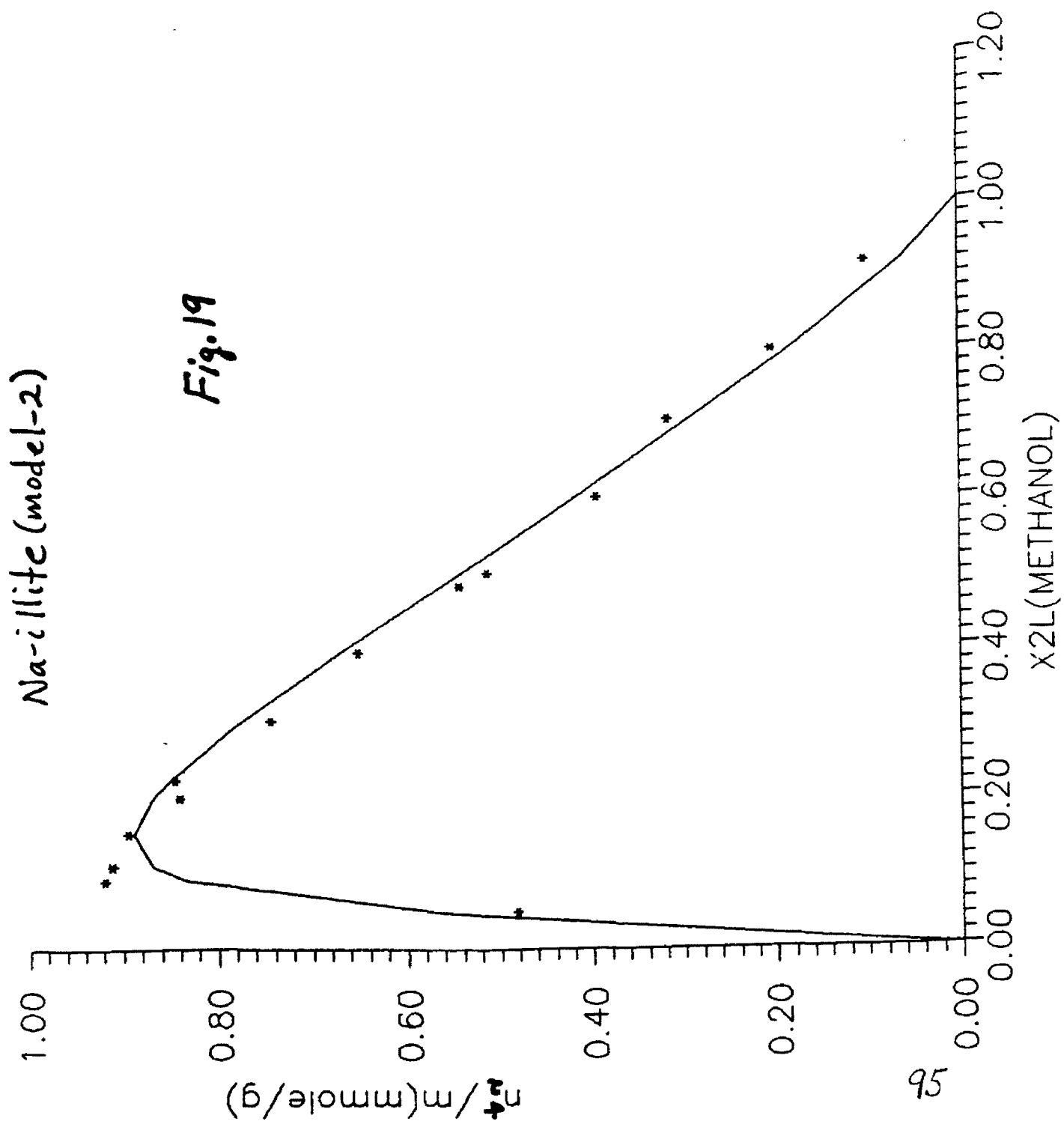




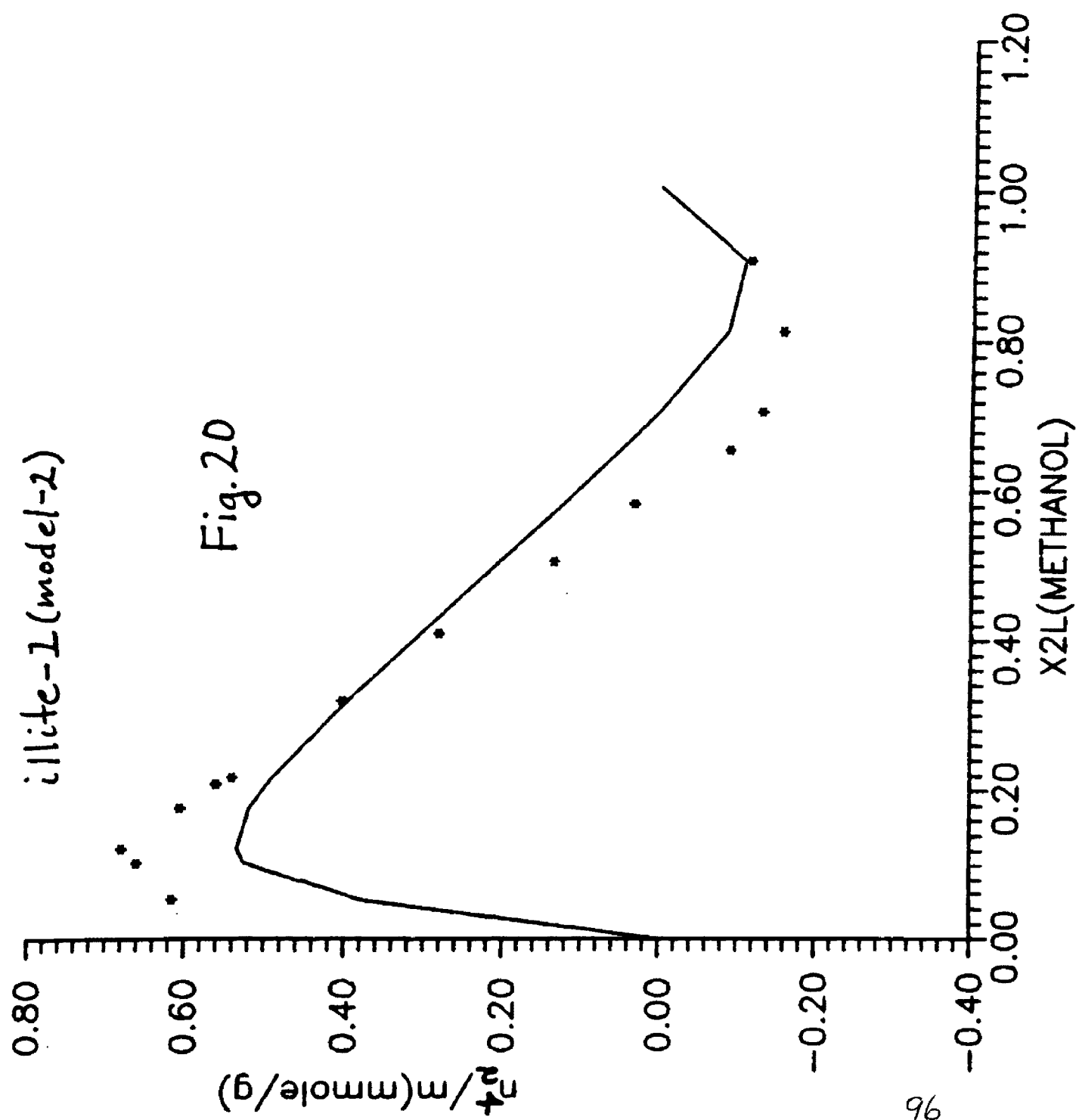


93

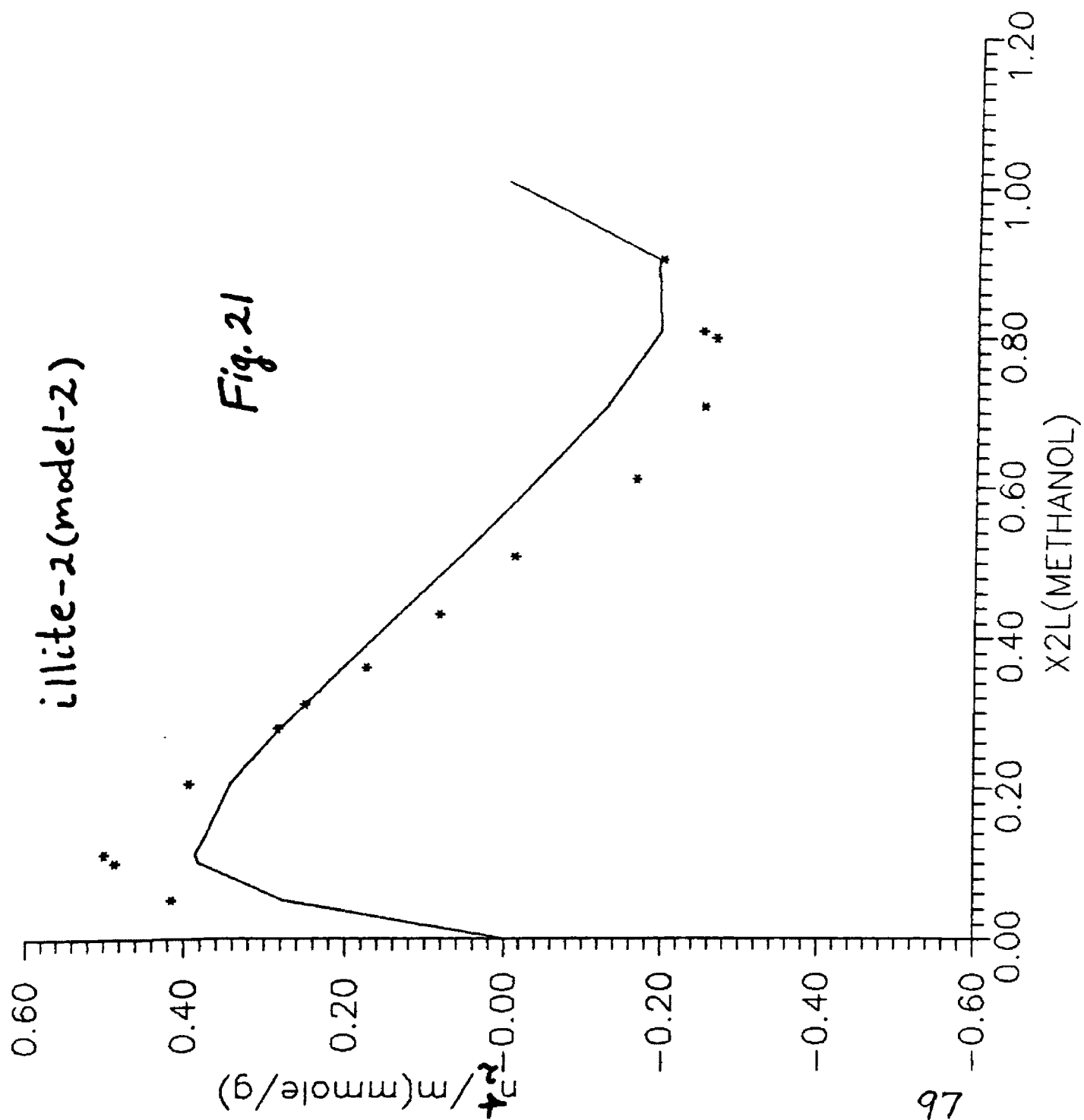


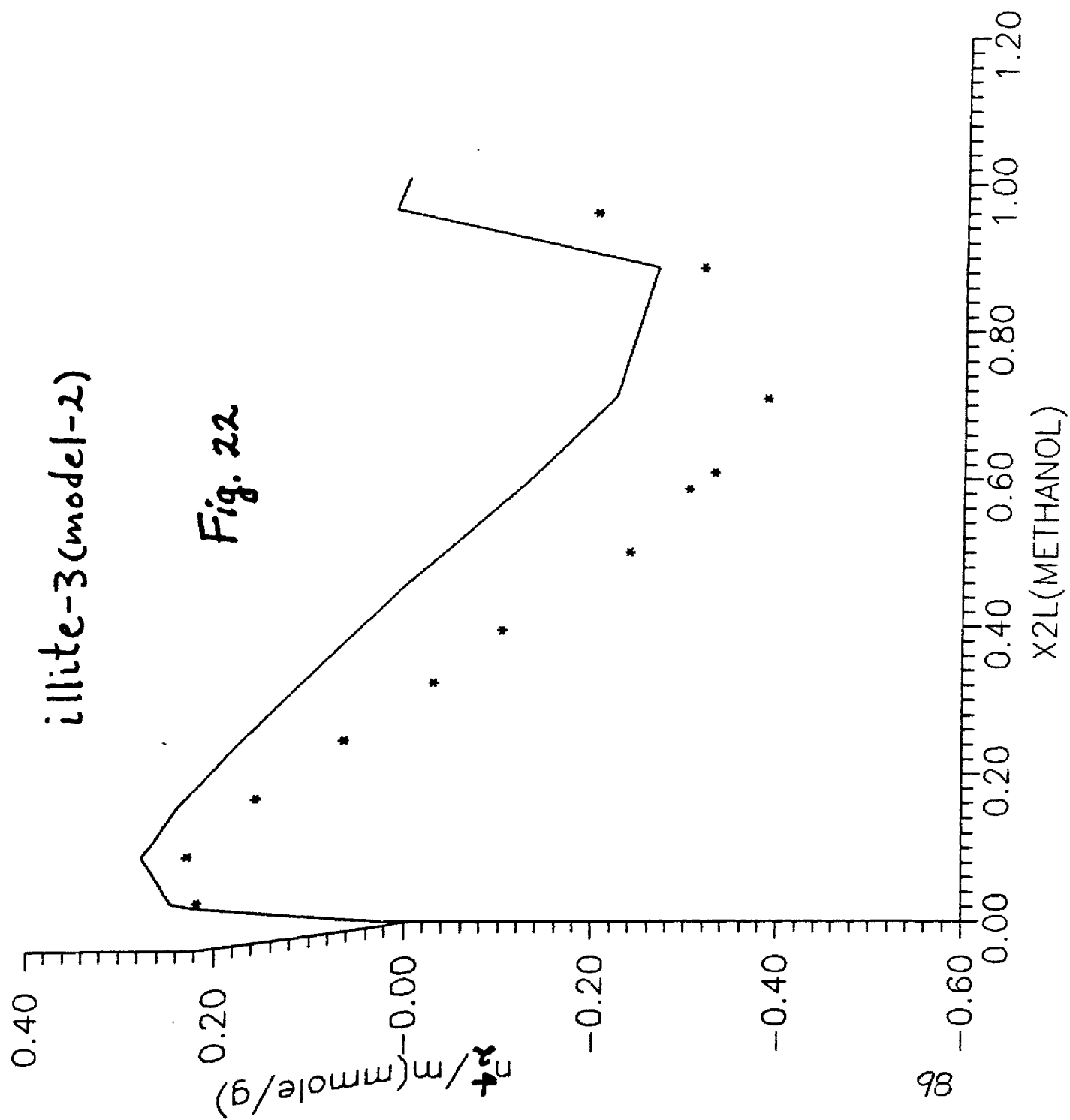


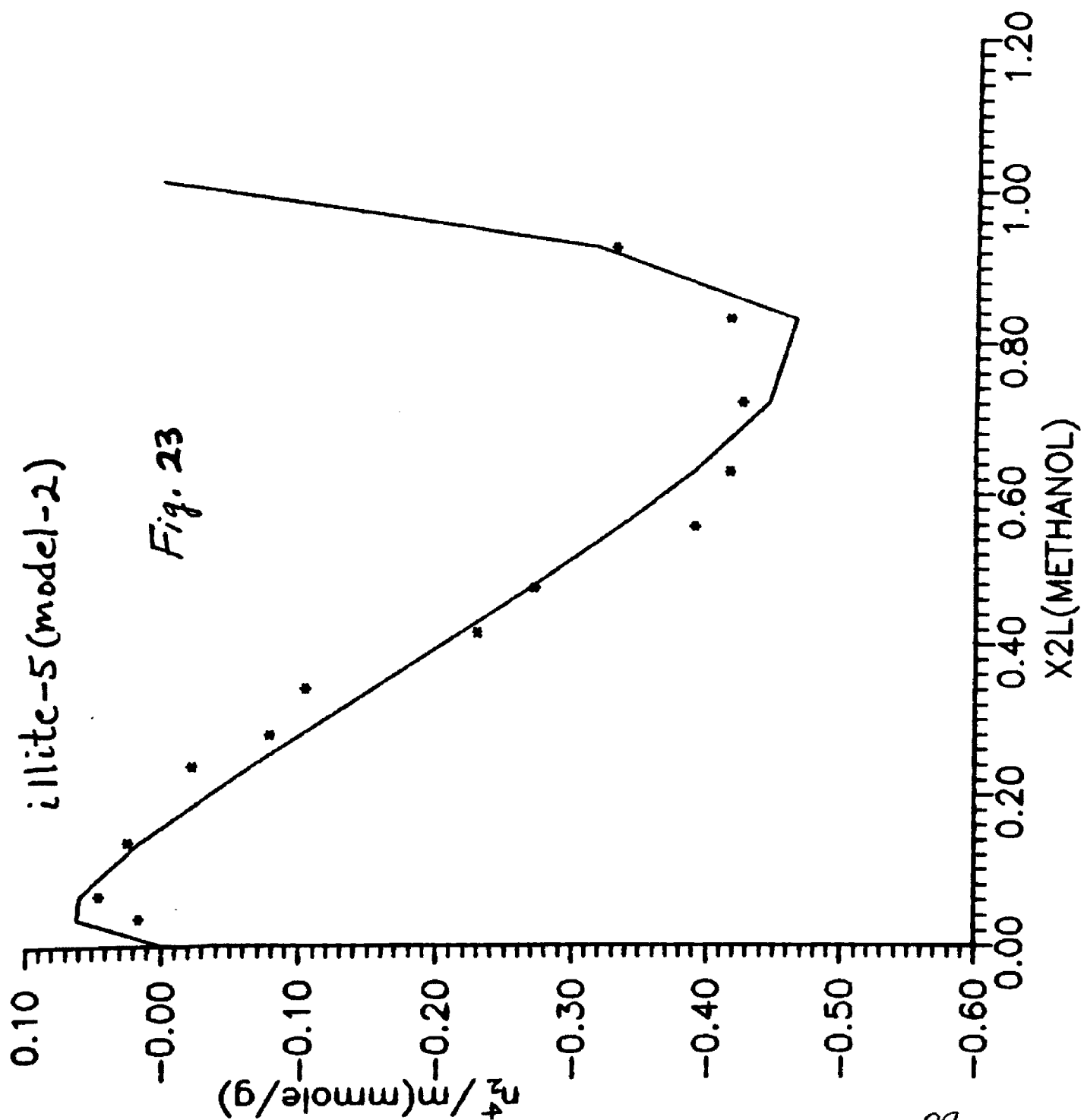


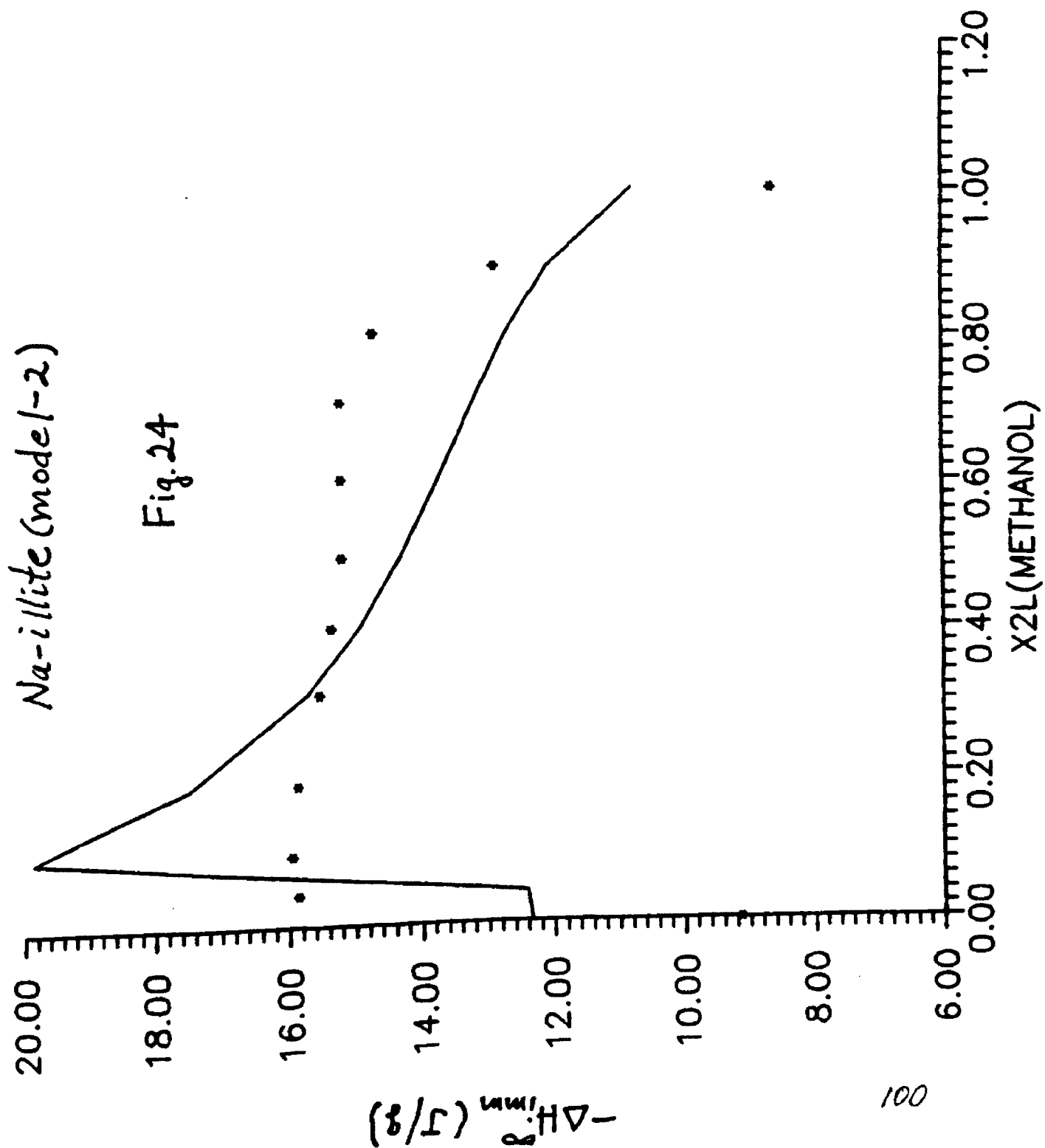


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100

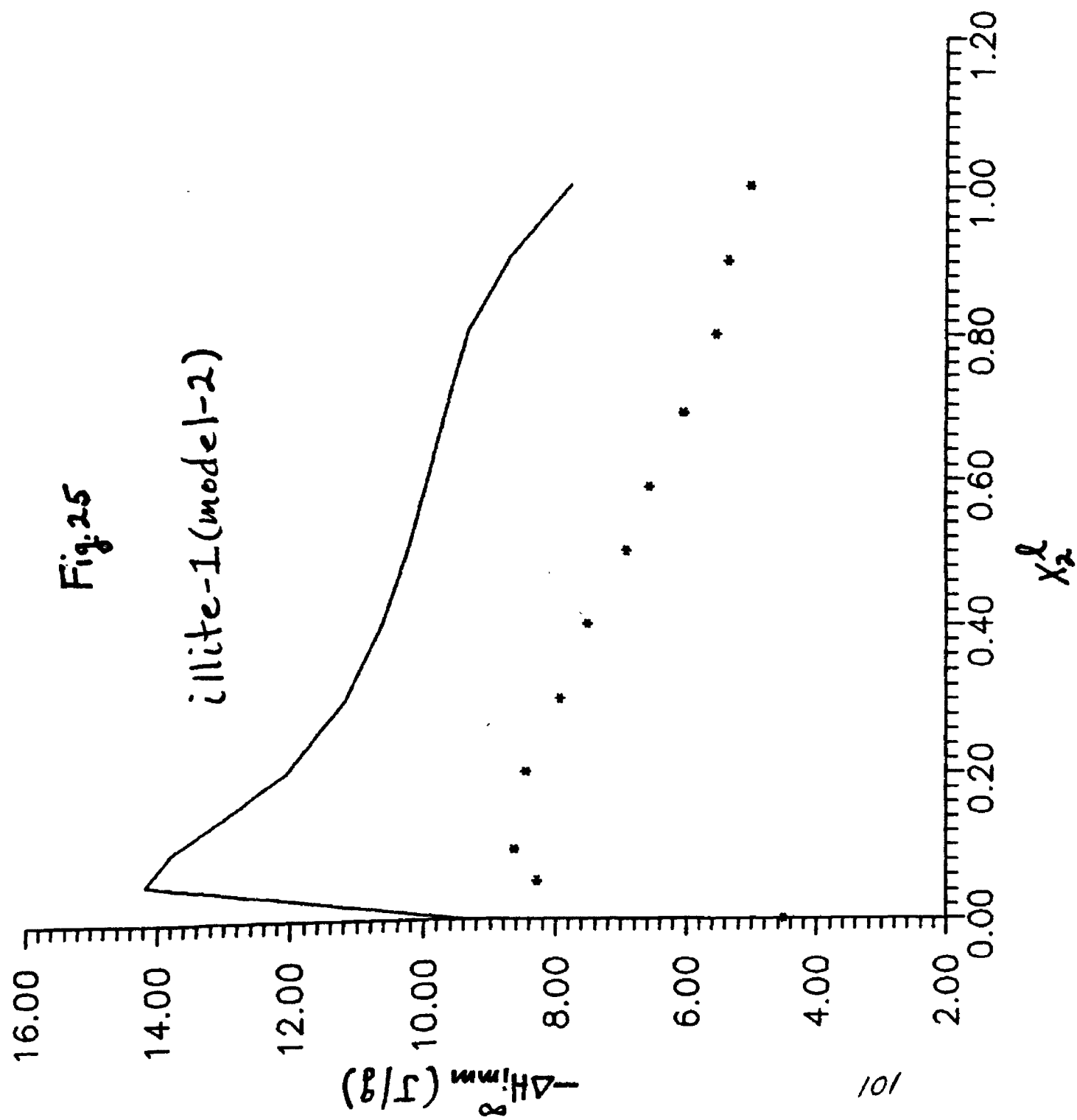
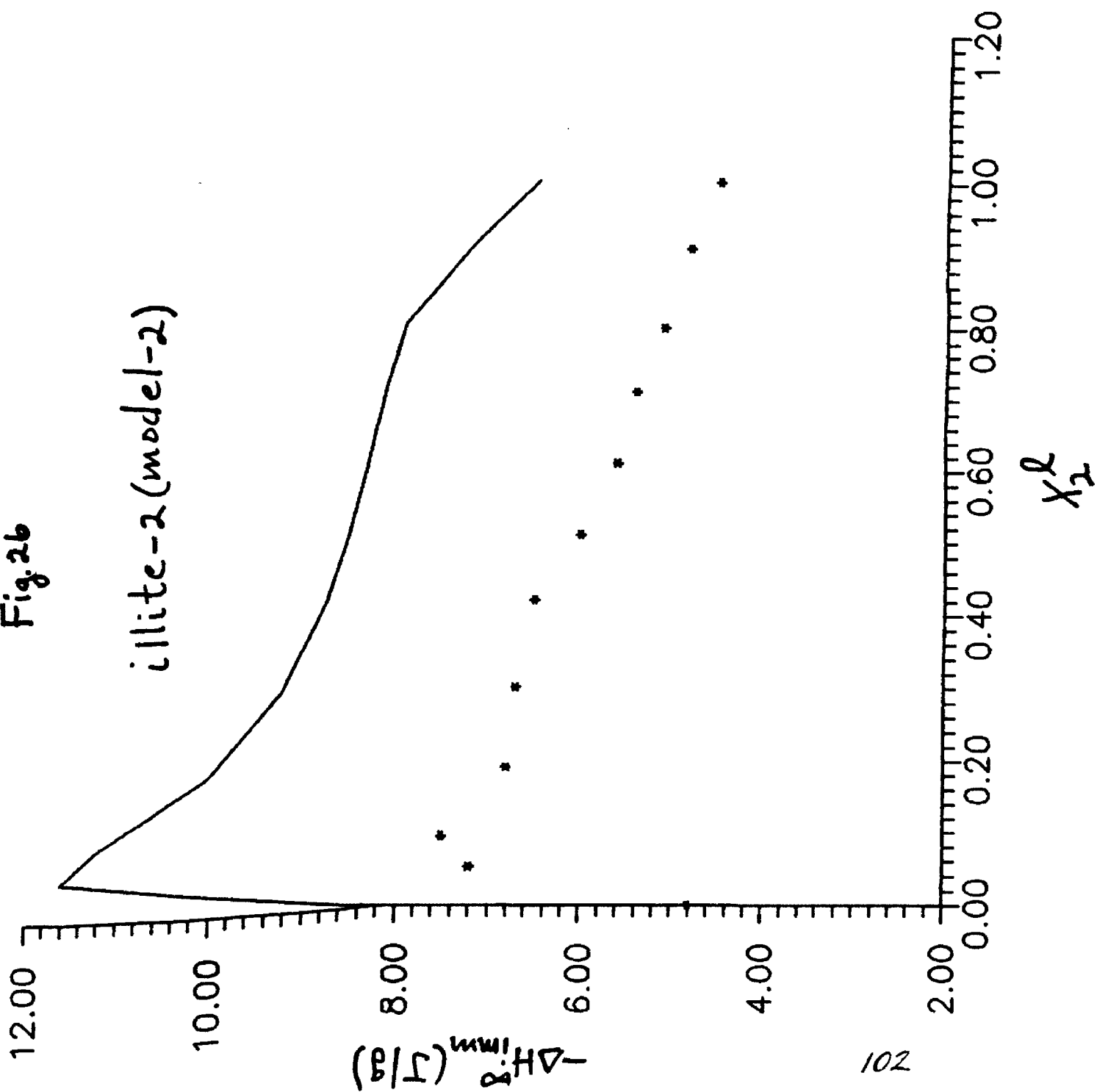
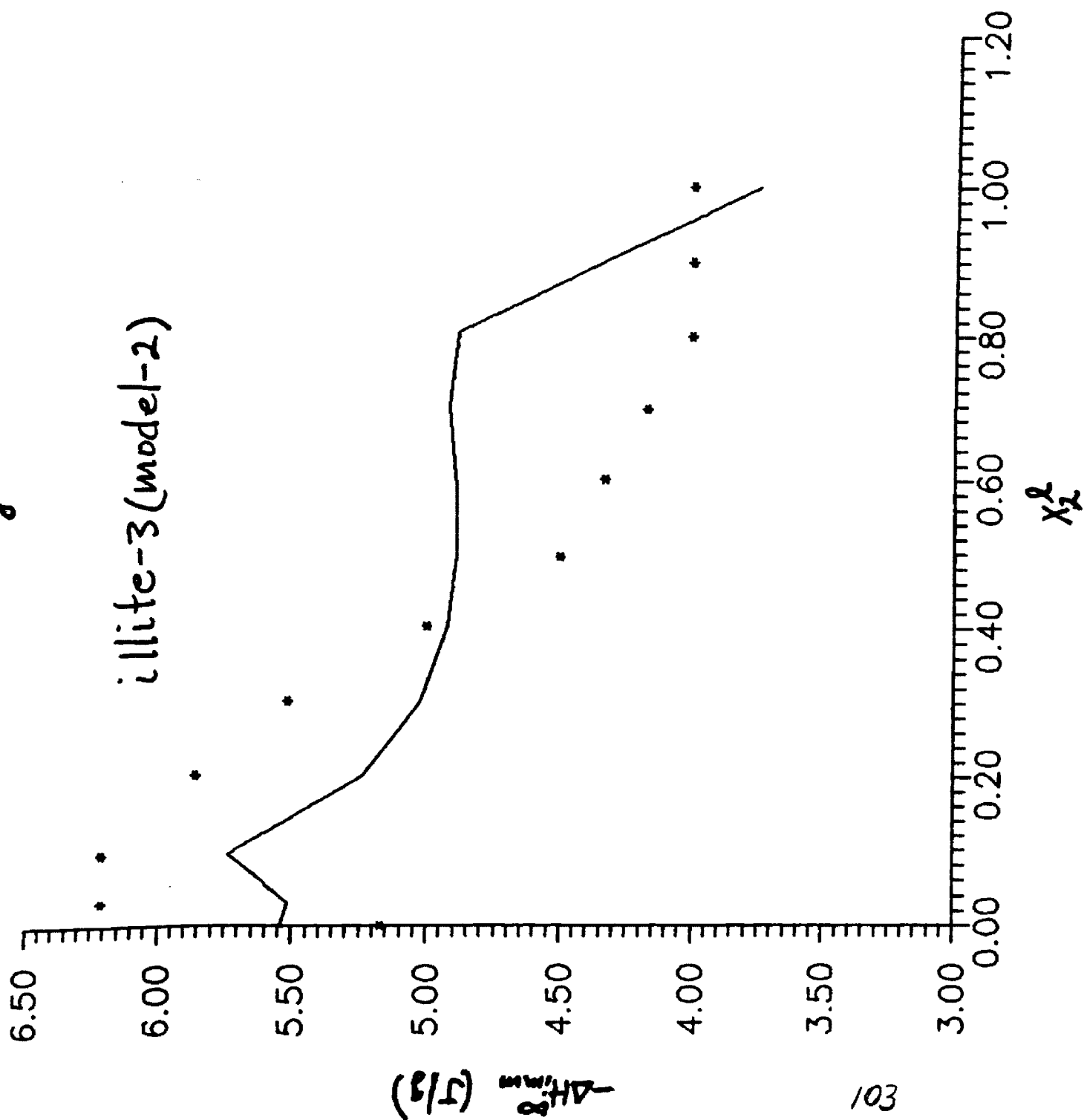


Fig. 26

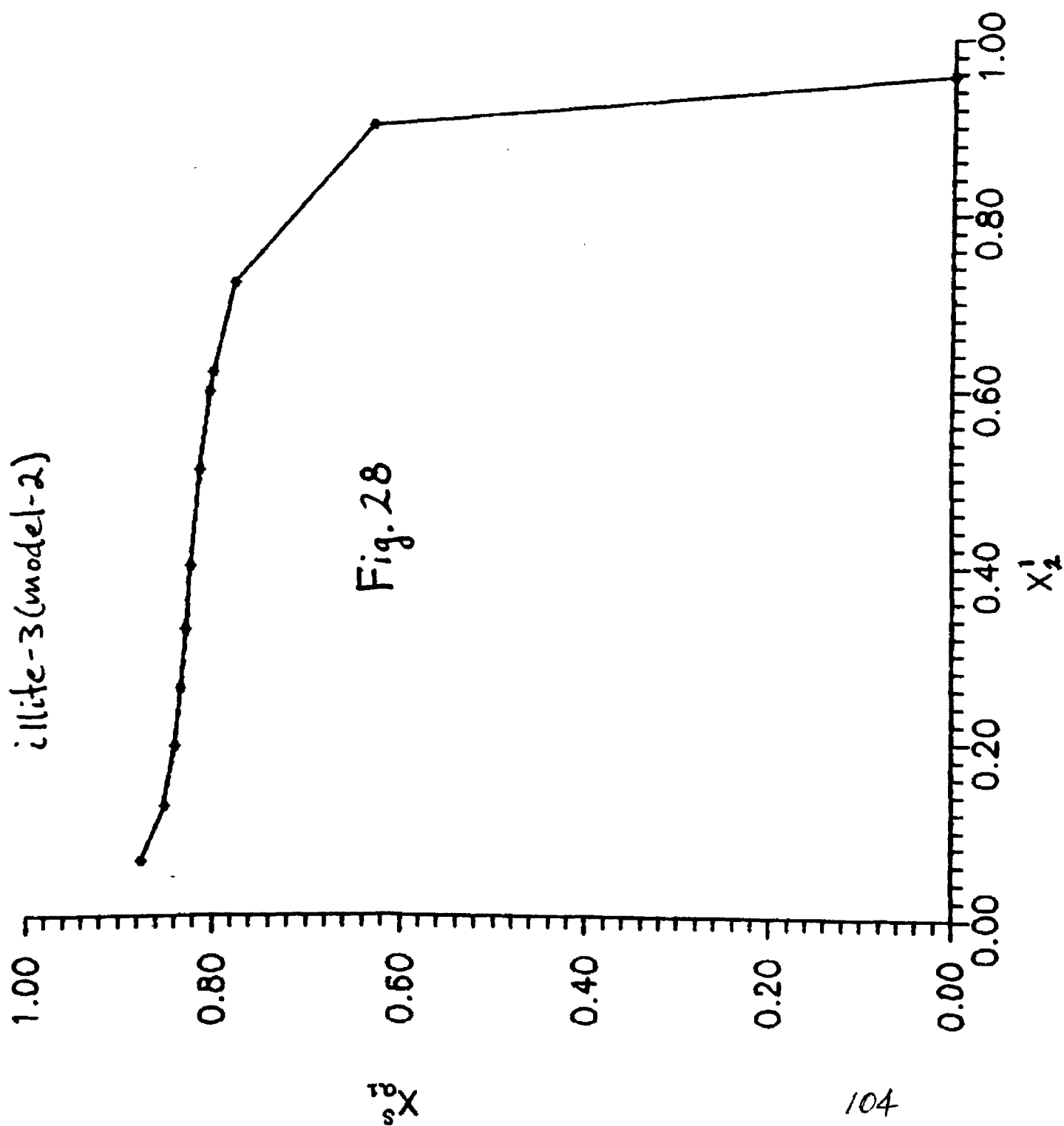


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Fig. 27







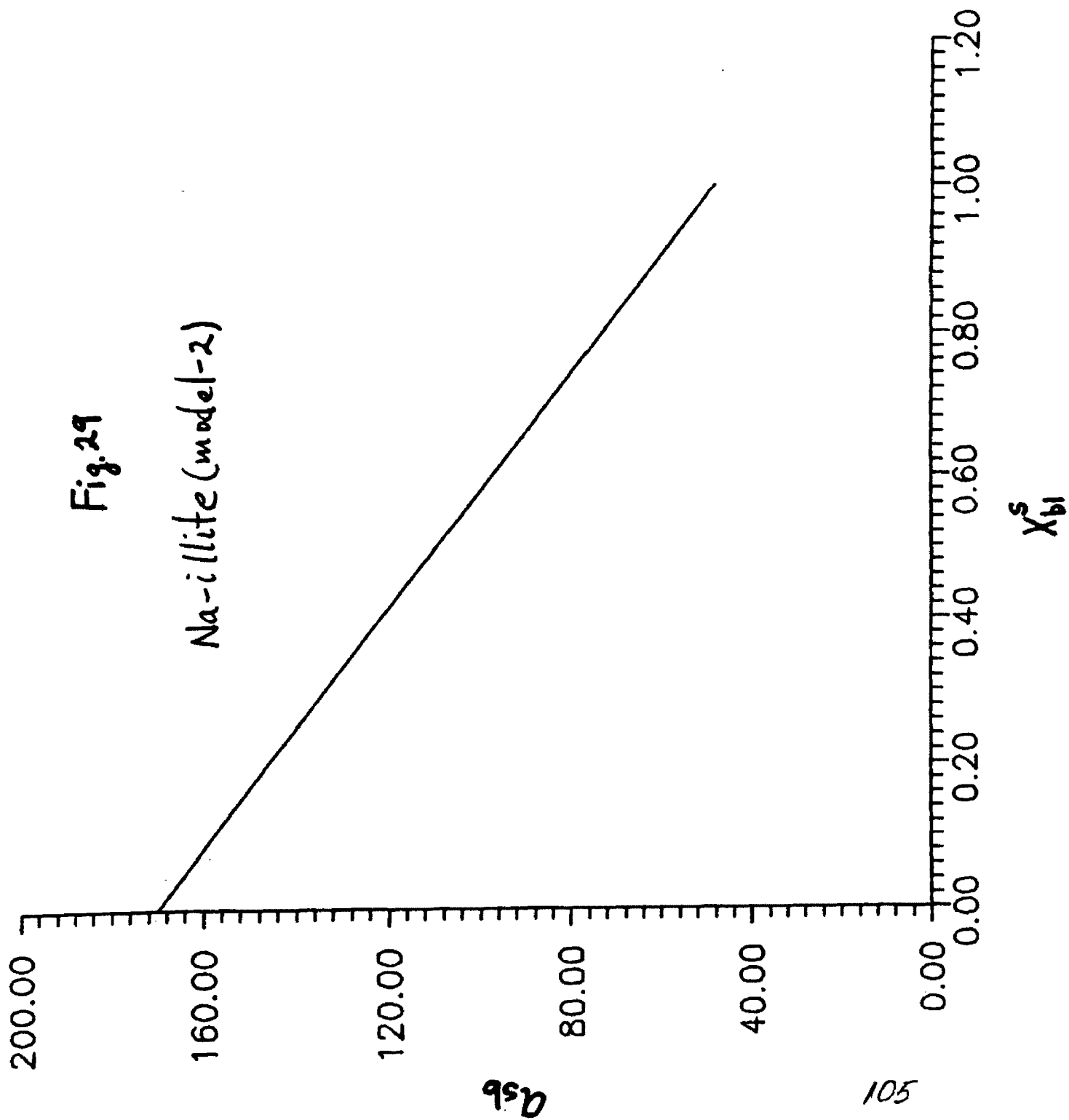
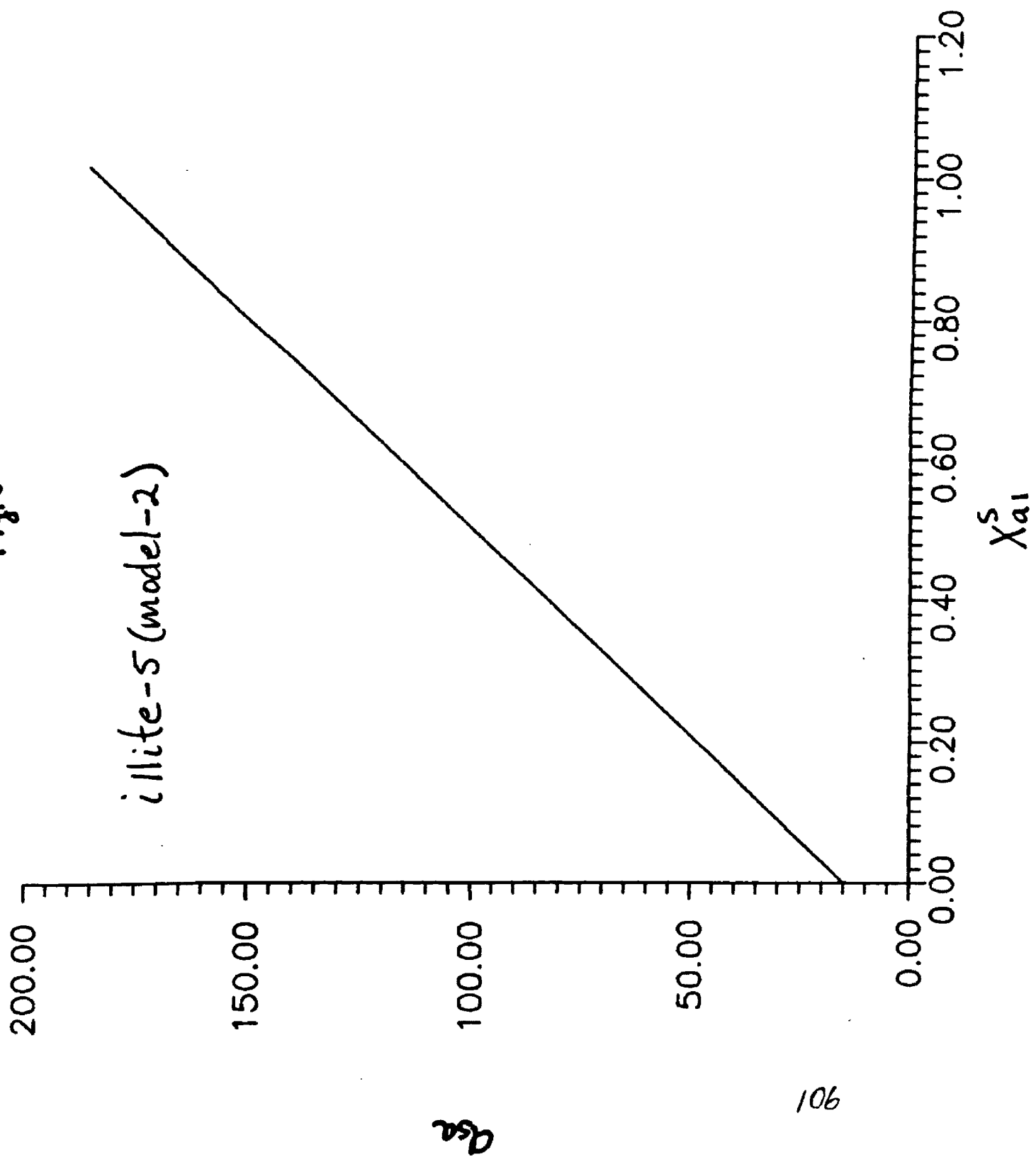
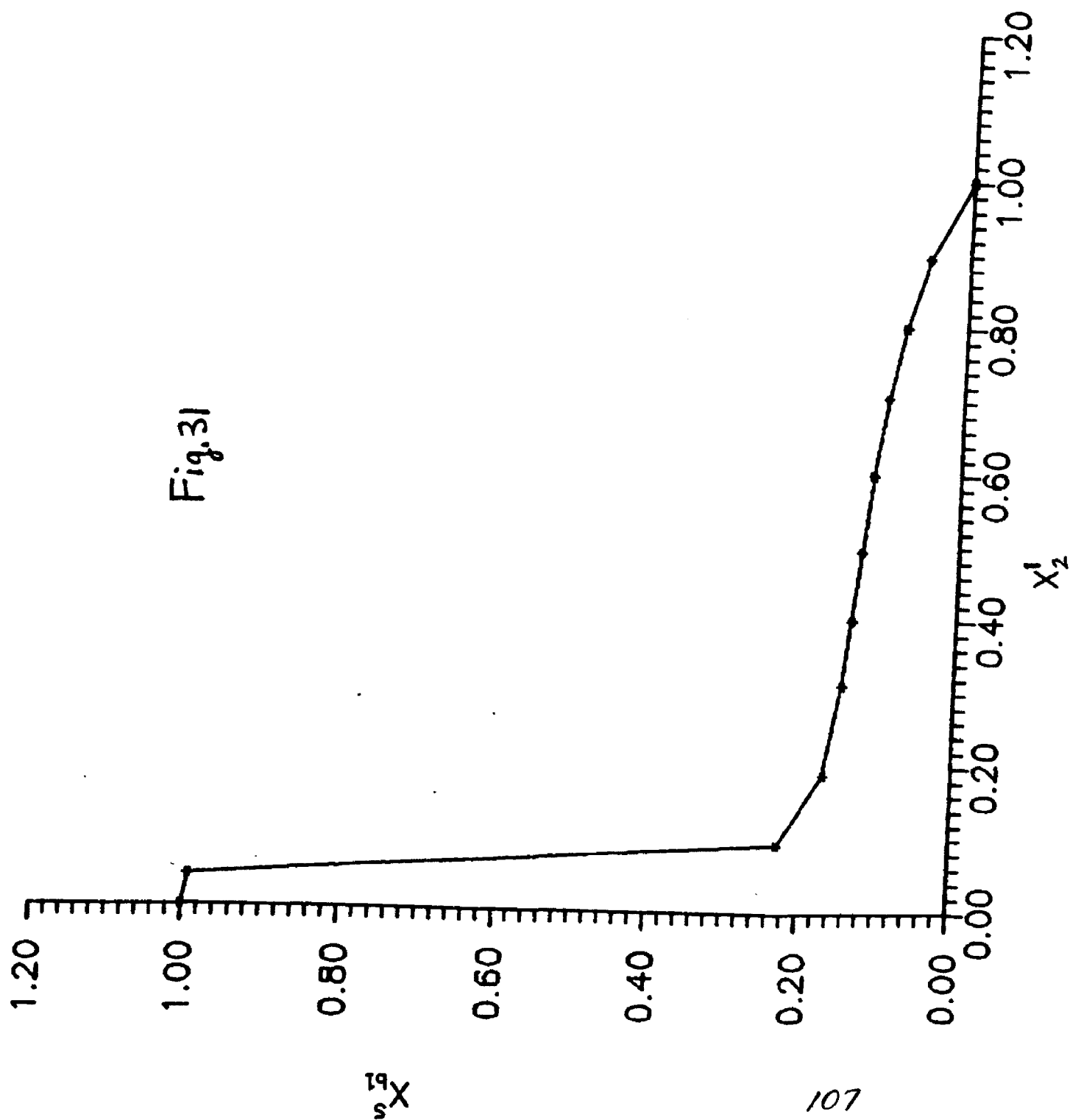
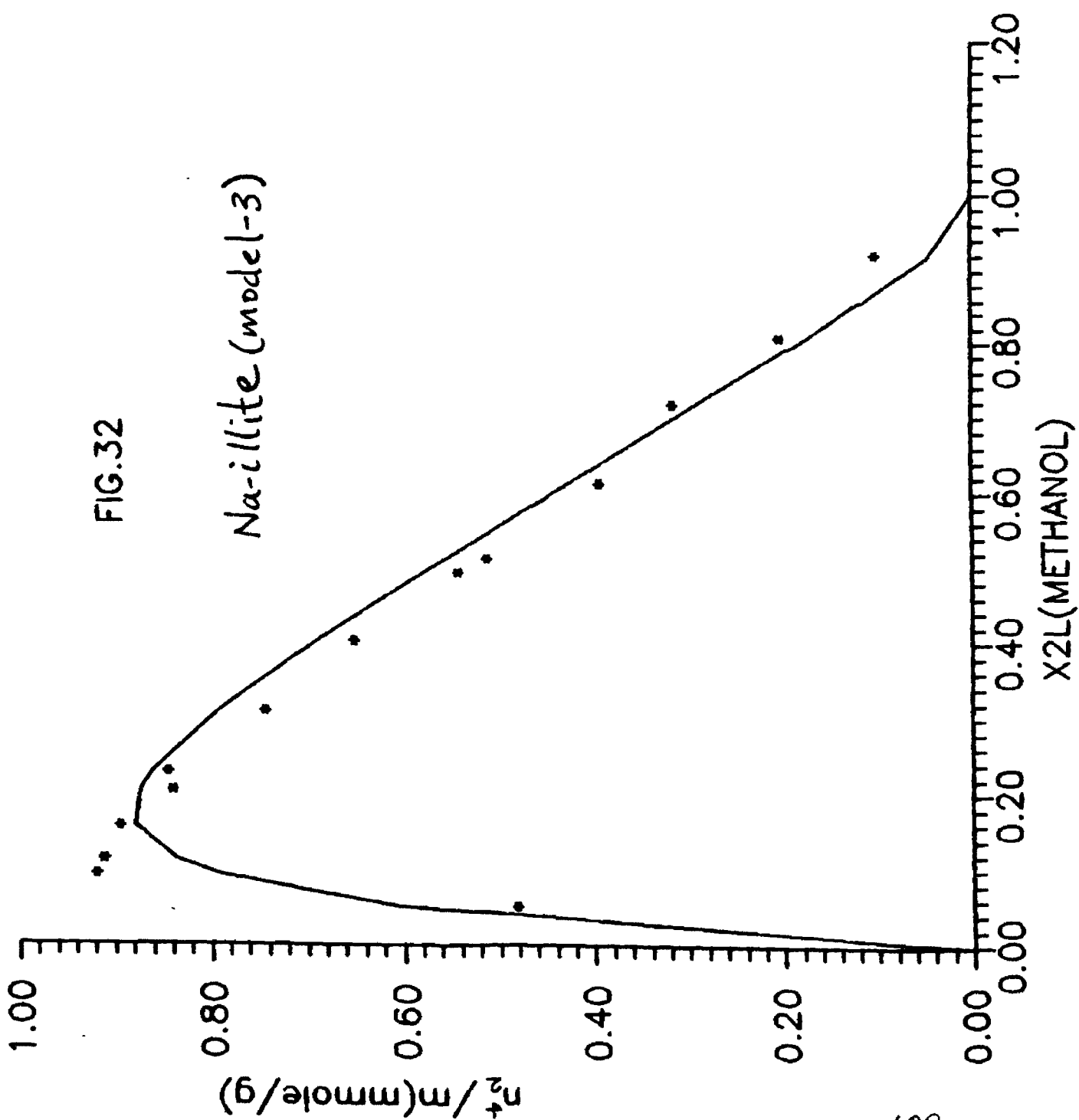


Fig. 30

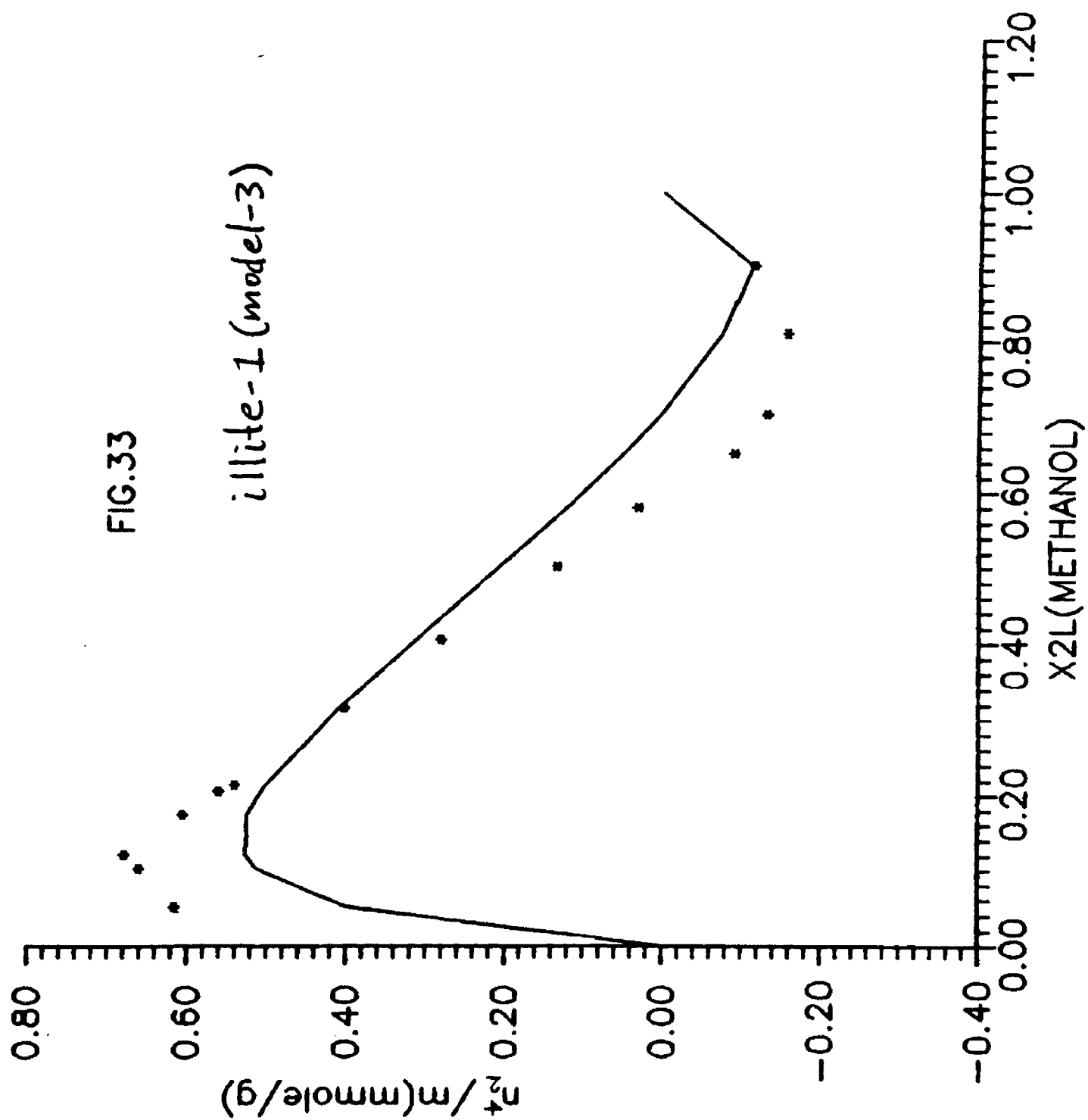


901

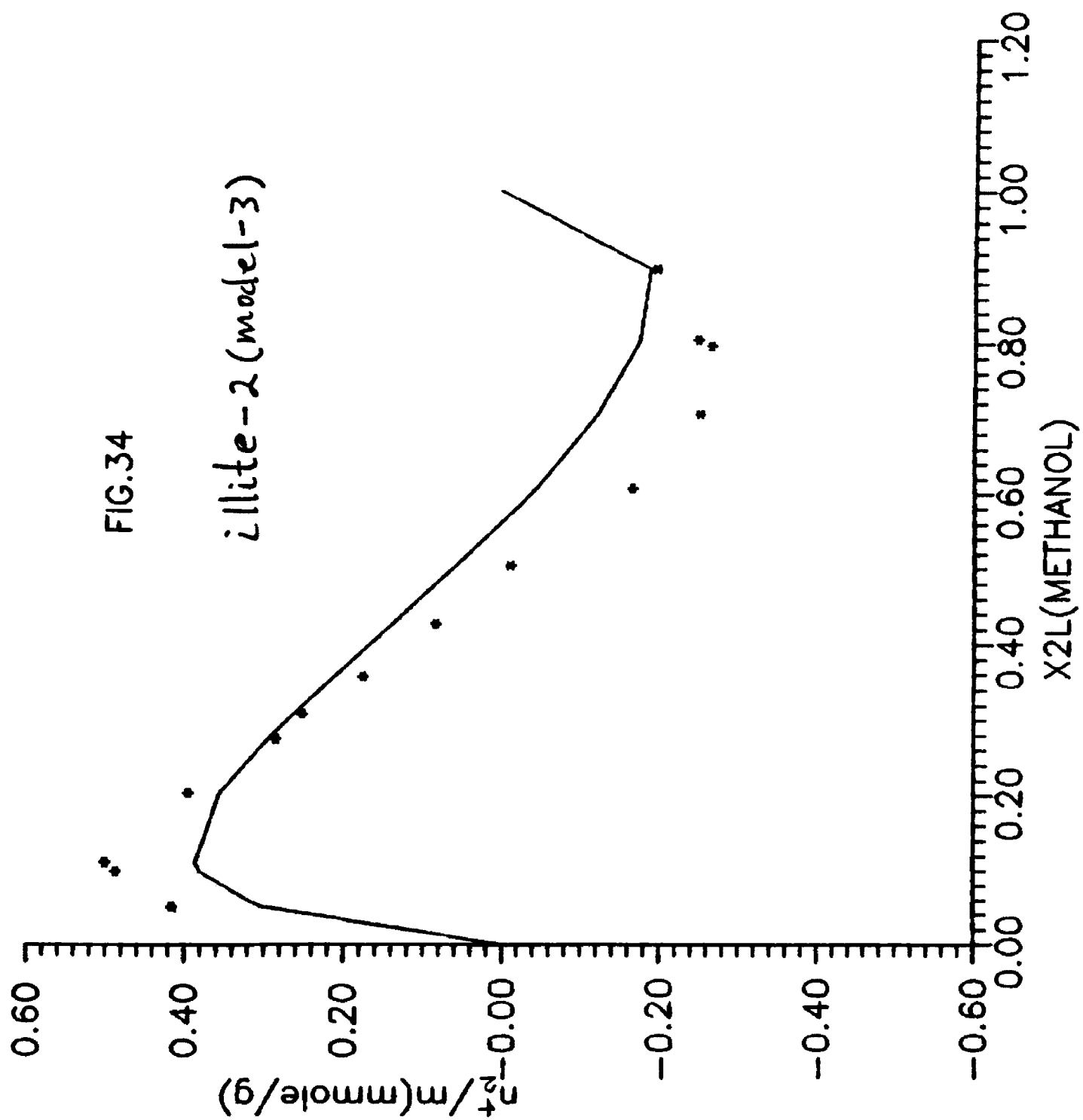




108



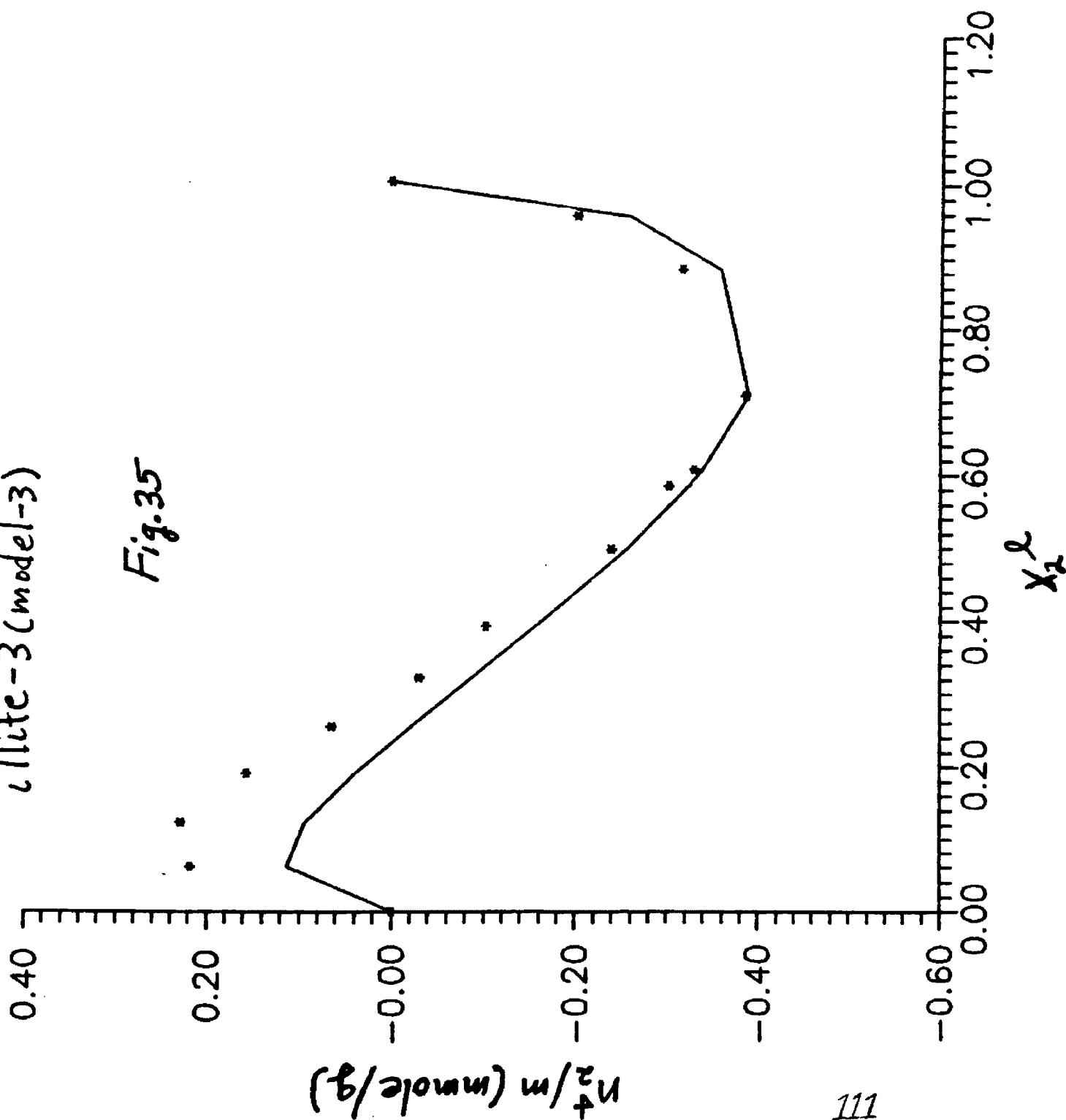
109



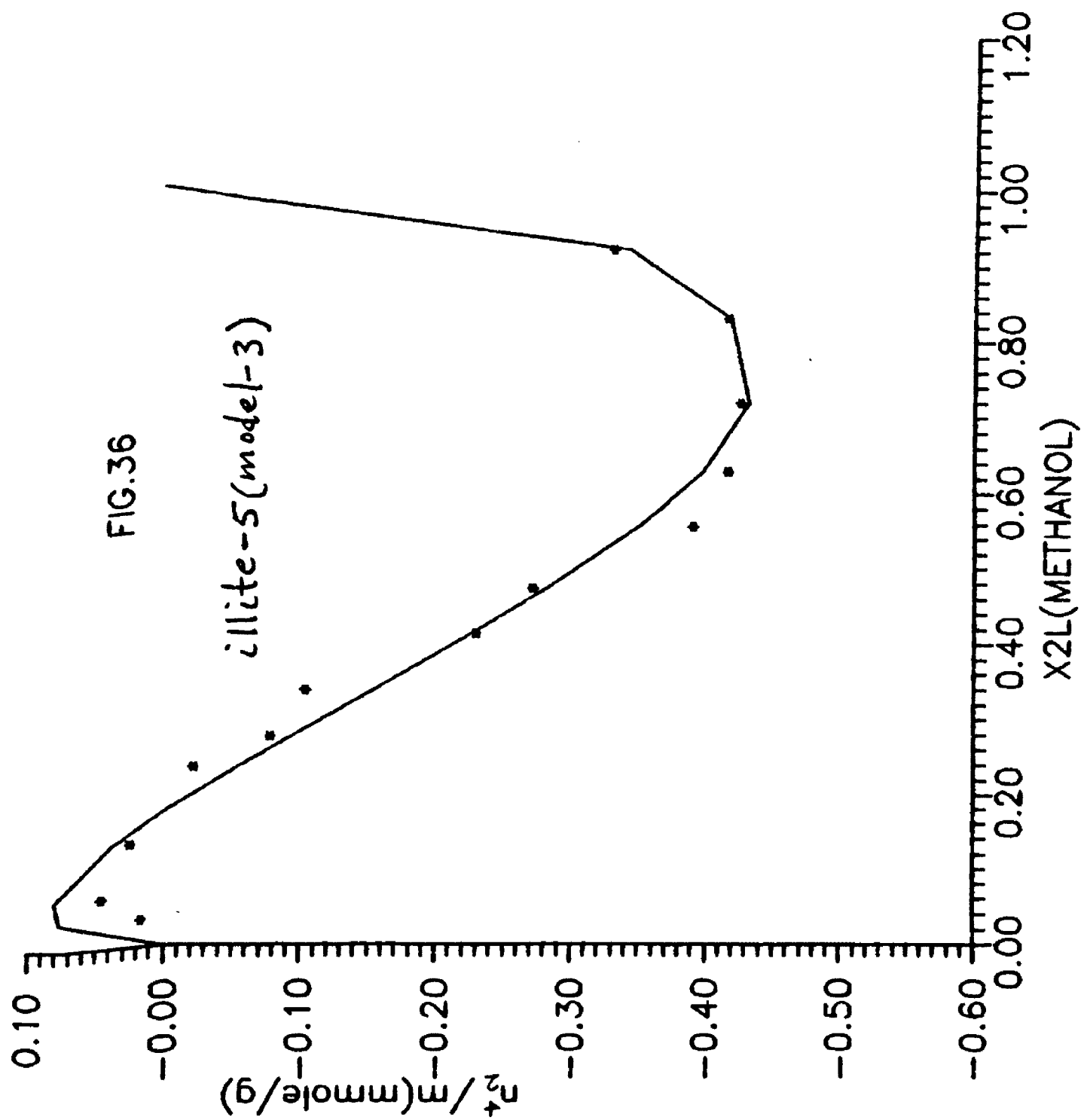
110

illite-3 (model-3)

Fig. 35

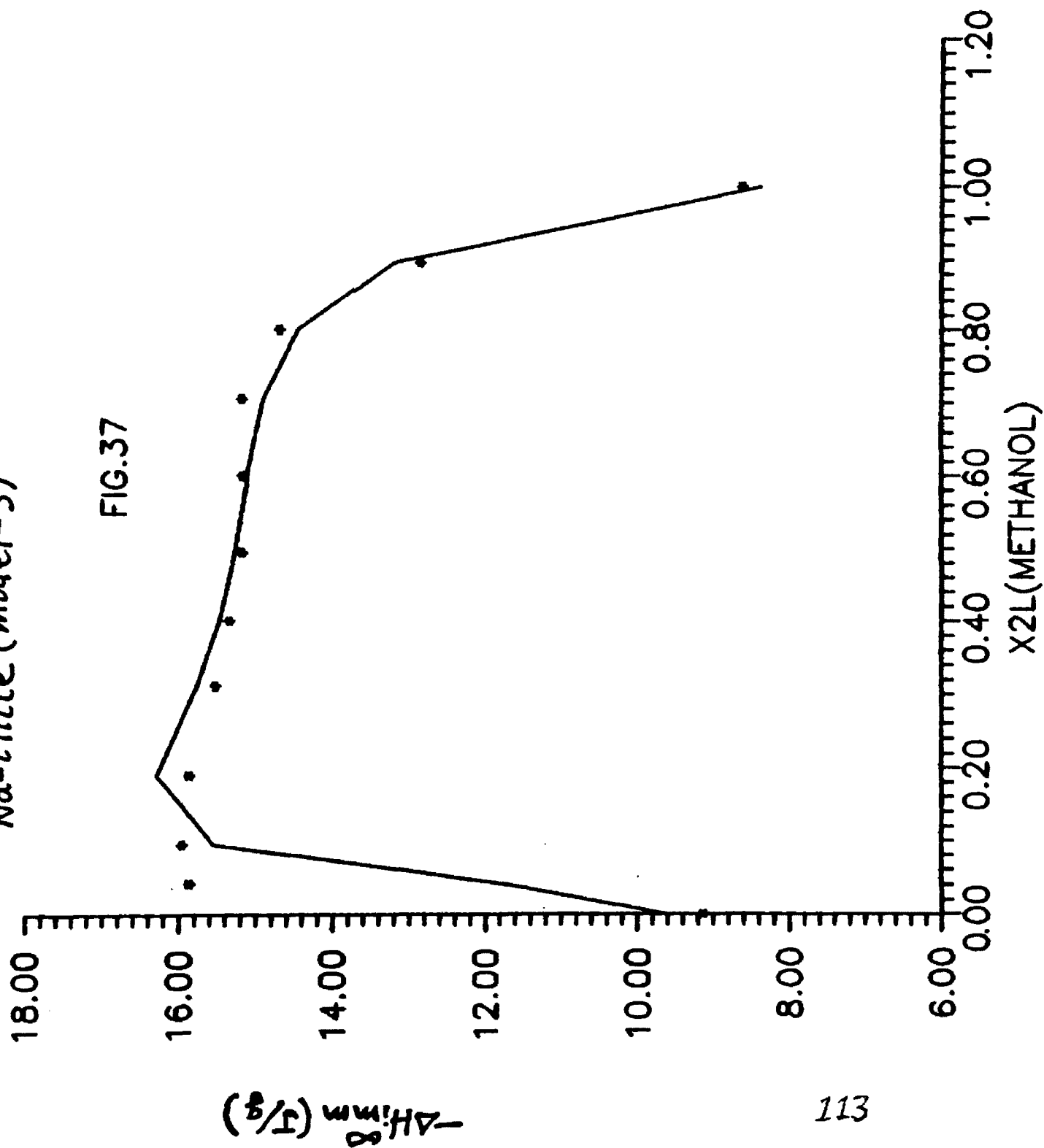






Na-illite (model-3)

FIG.37



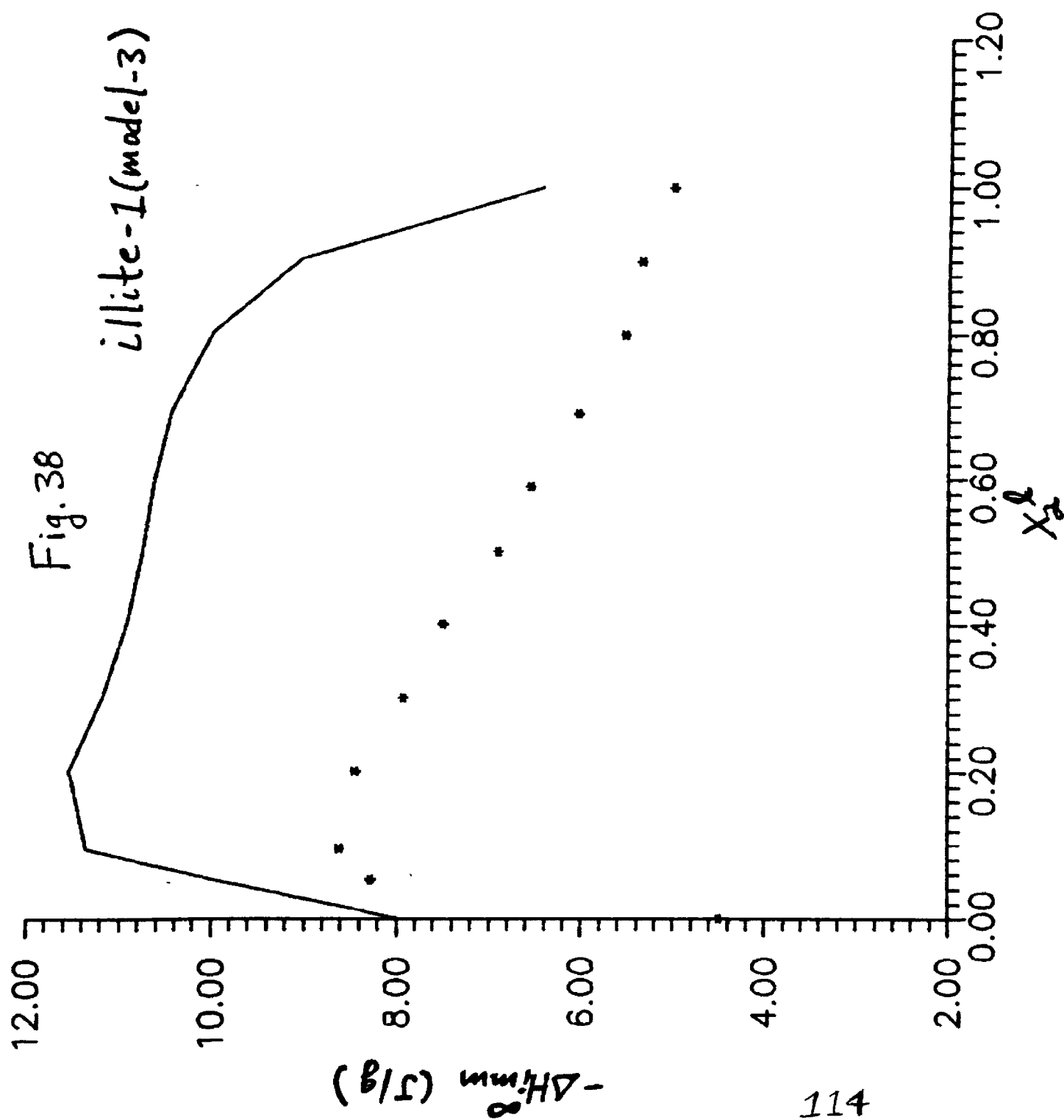


Fig. 39

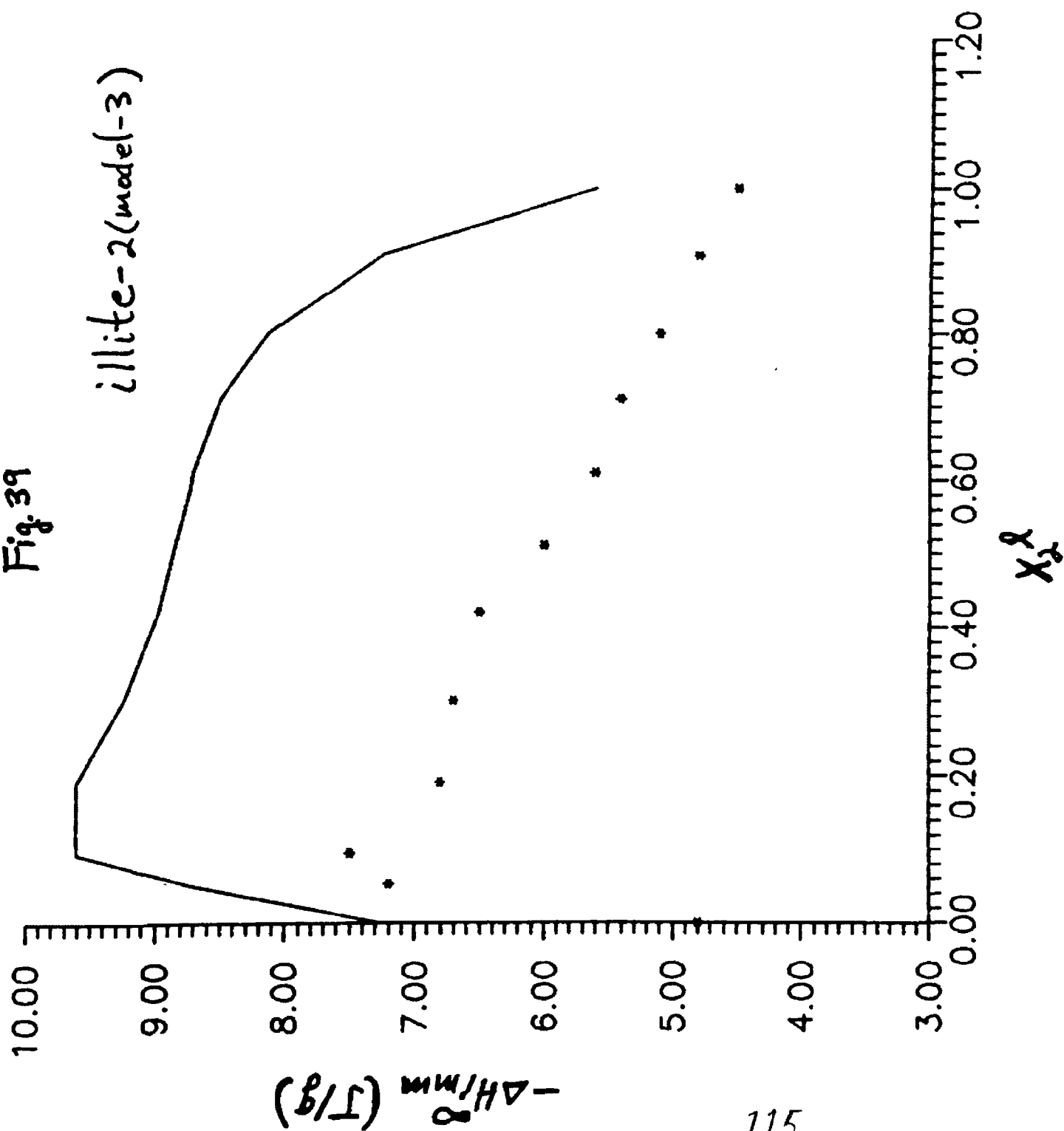
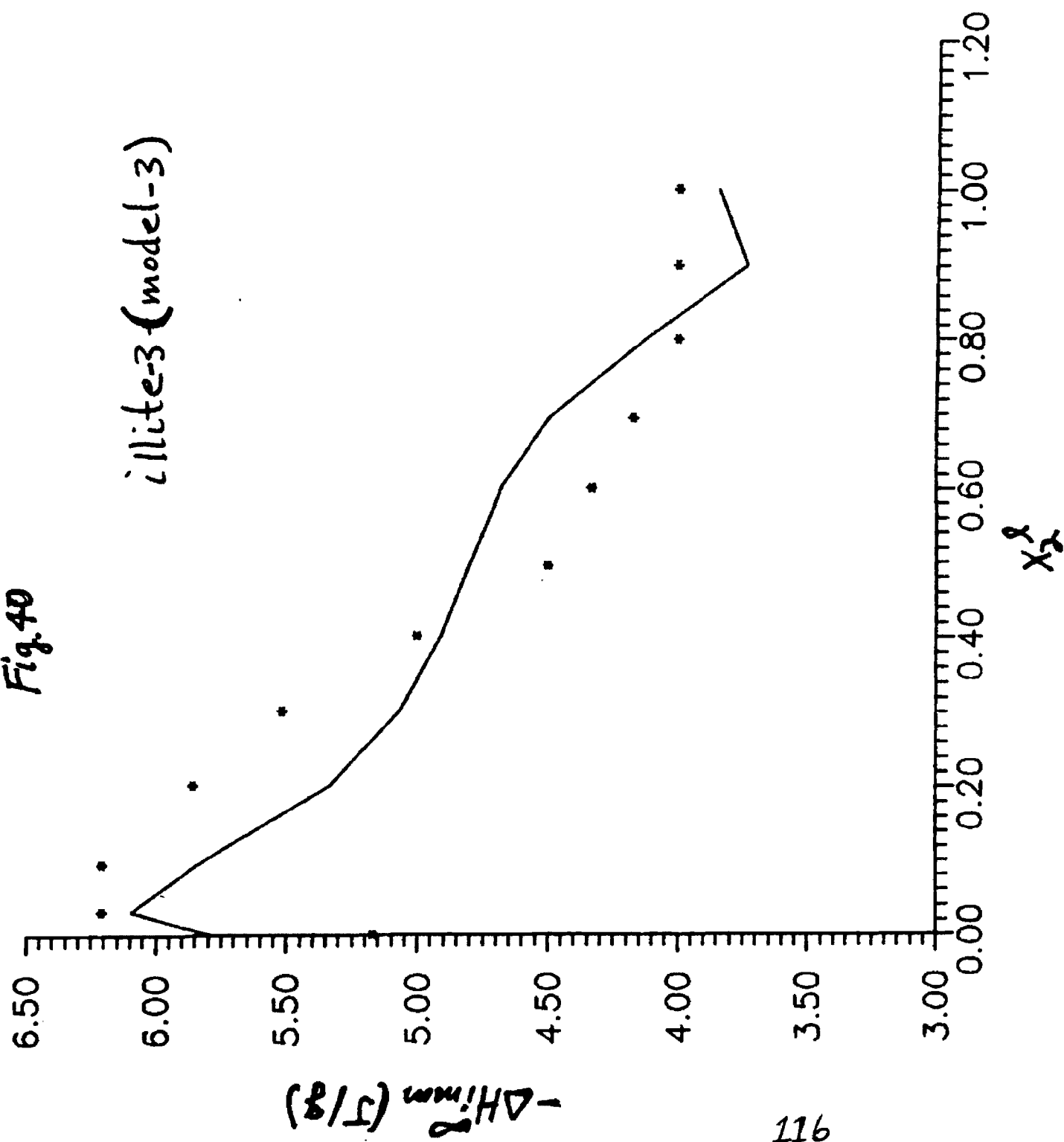
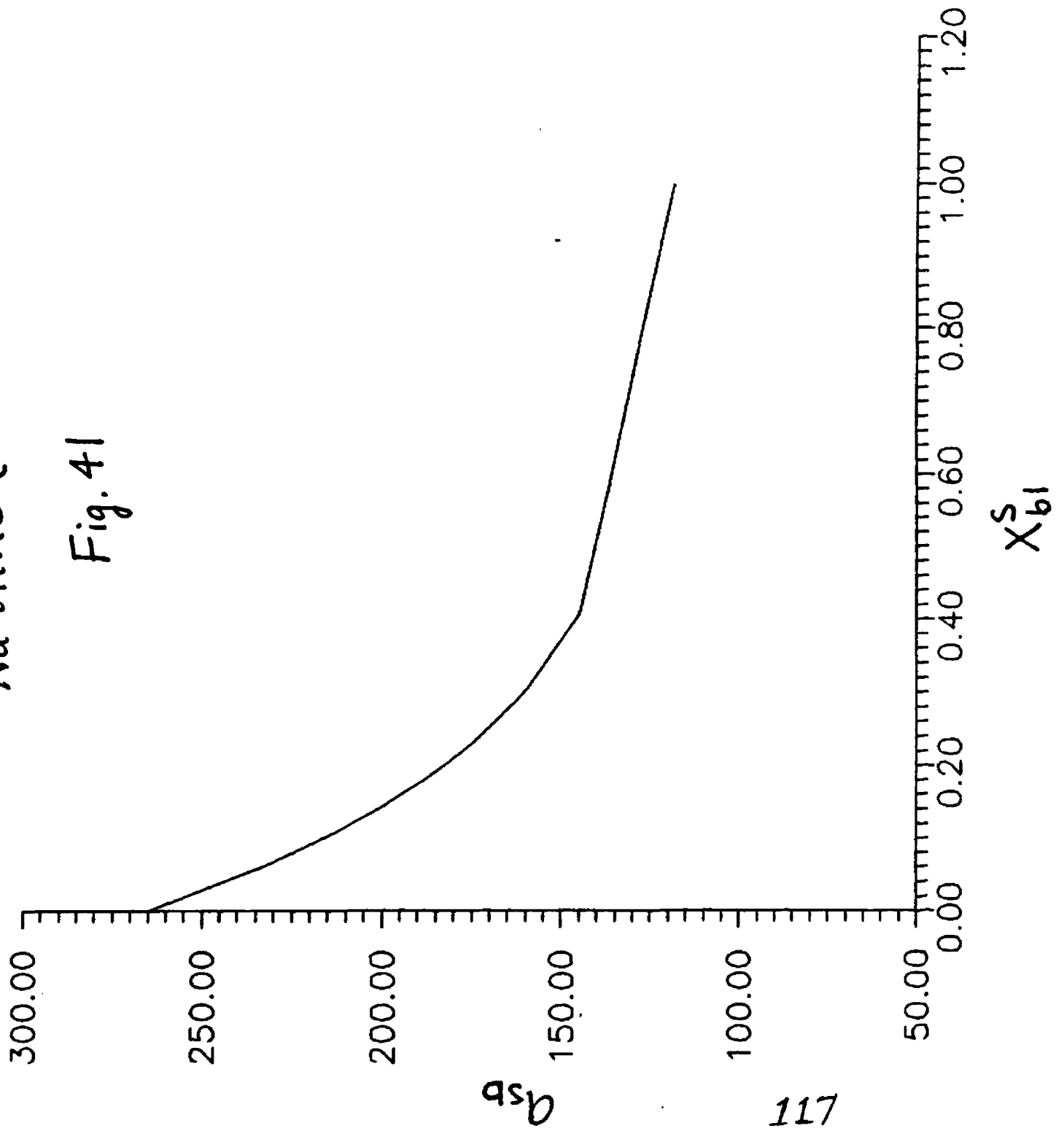


Fig. 40



Na-illite (model-3)

Fig. 41



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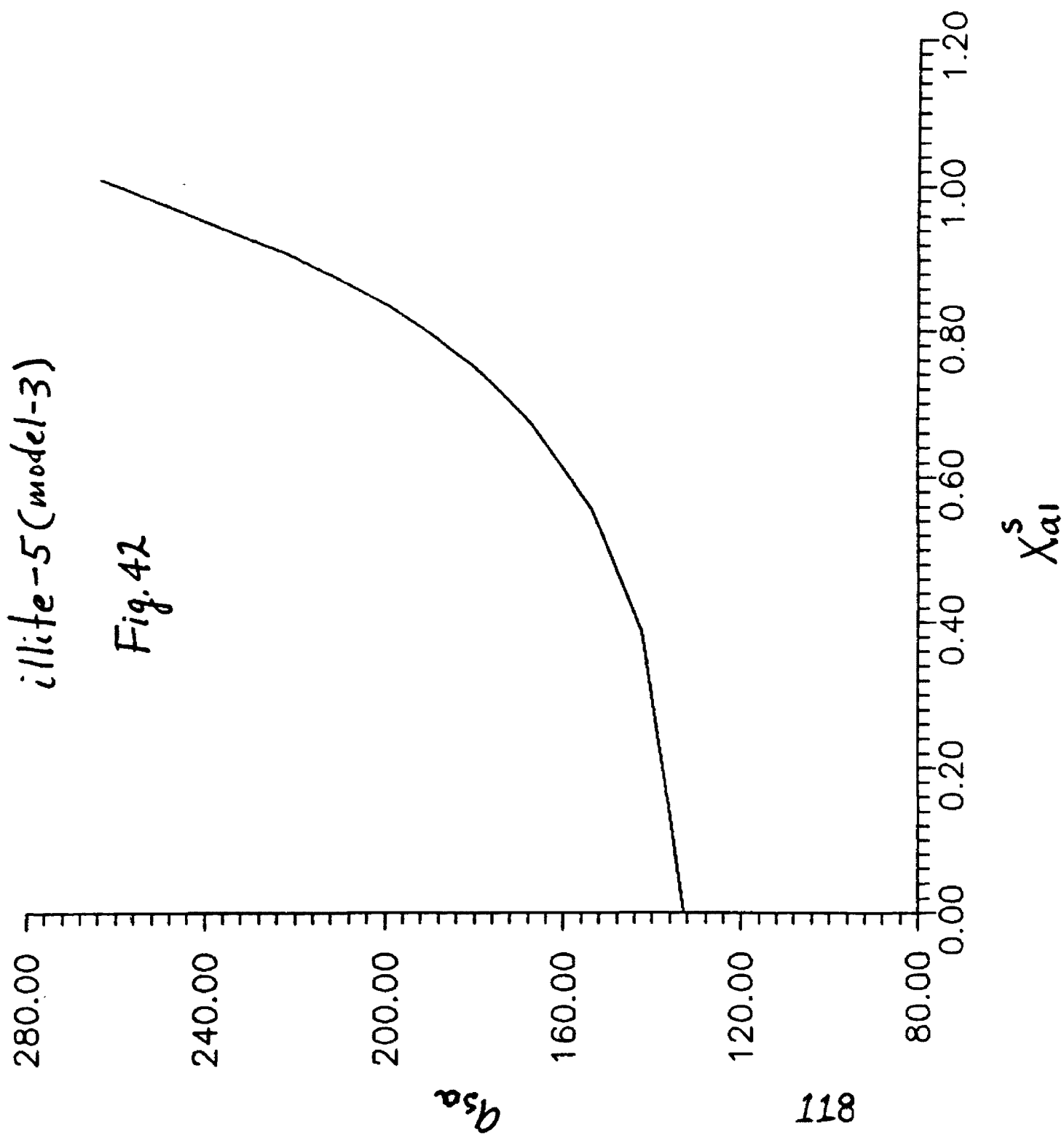
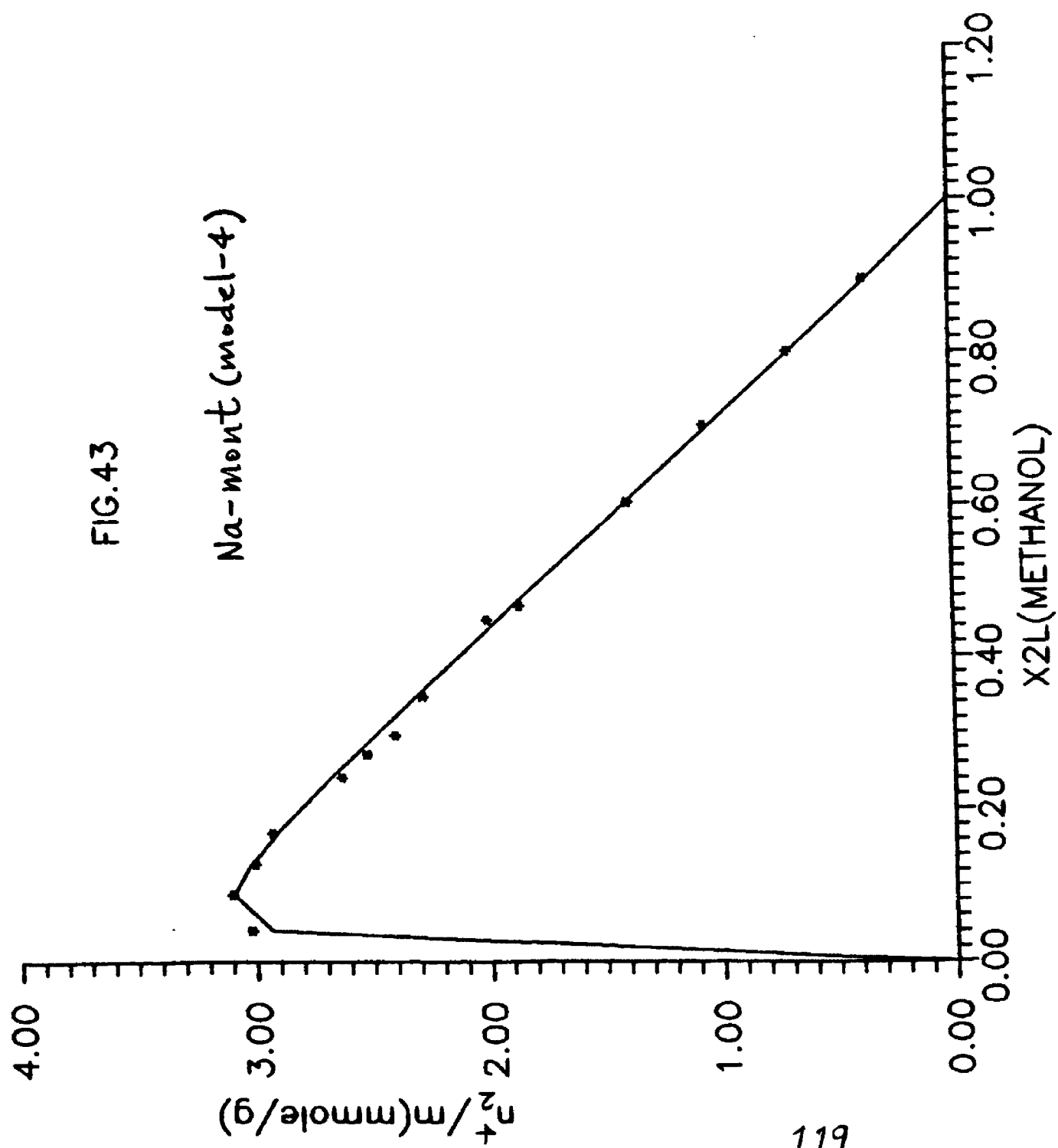
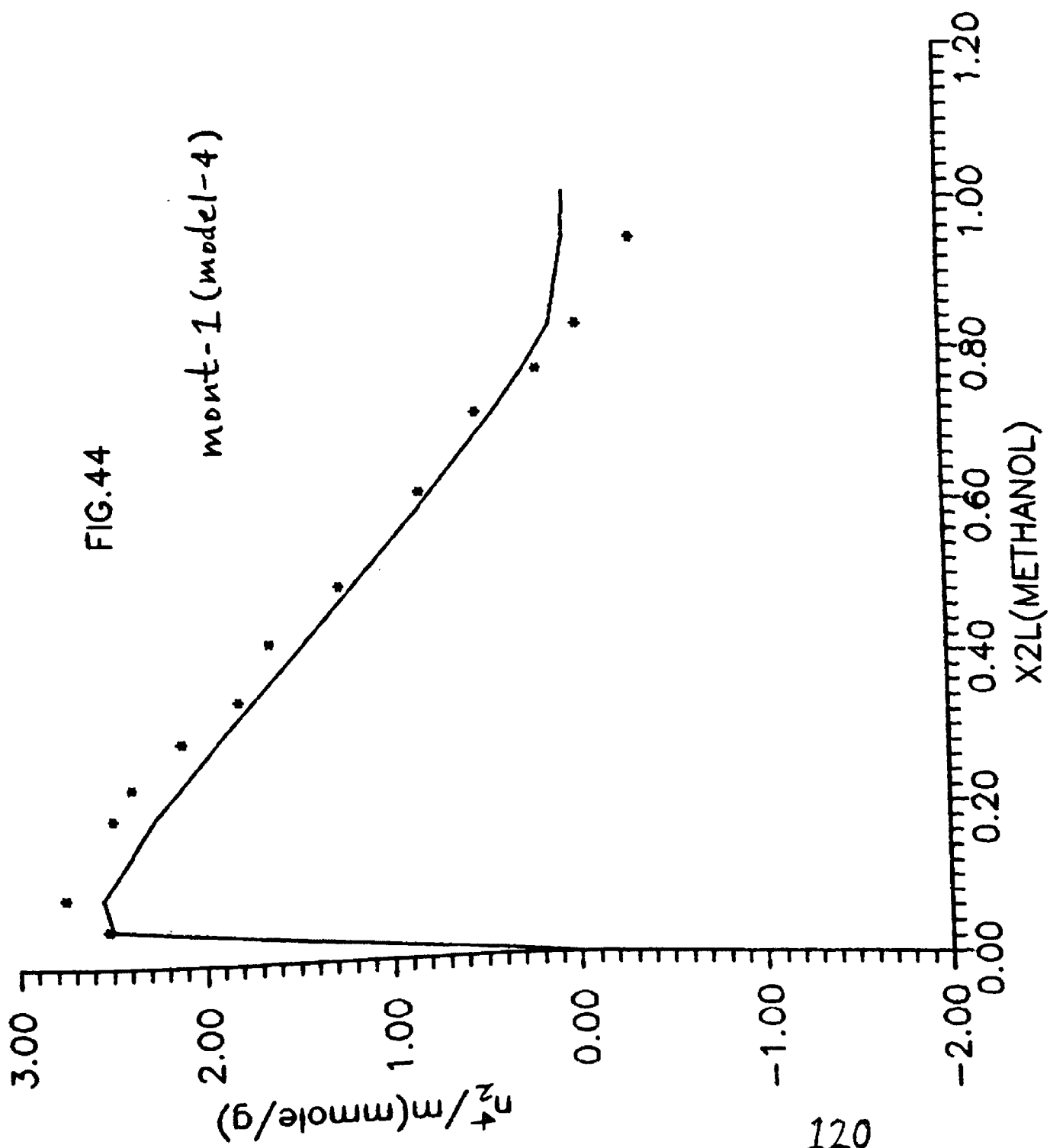
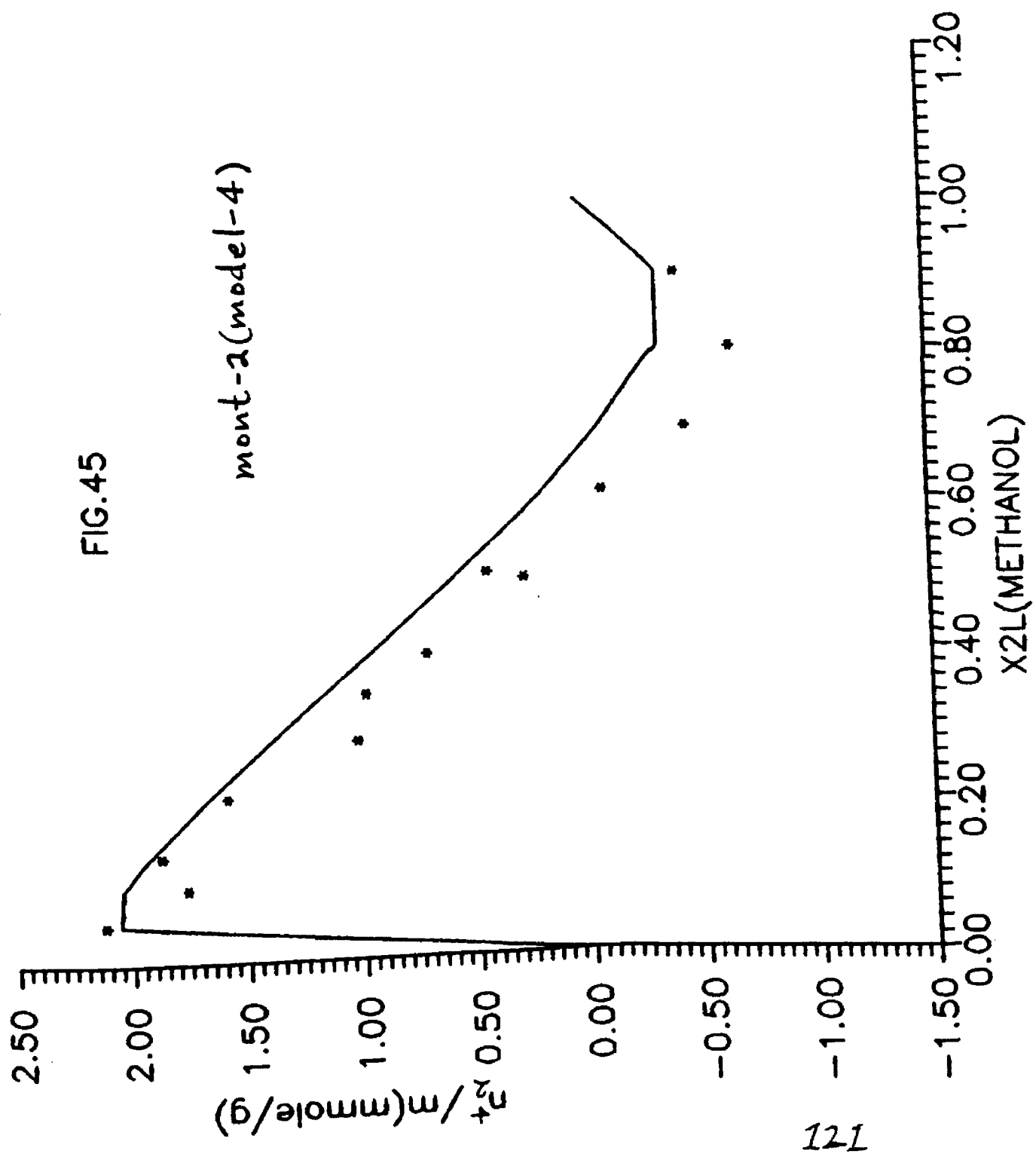


FIG. 43

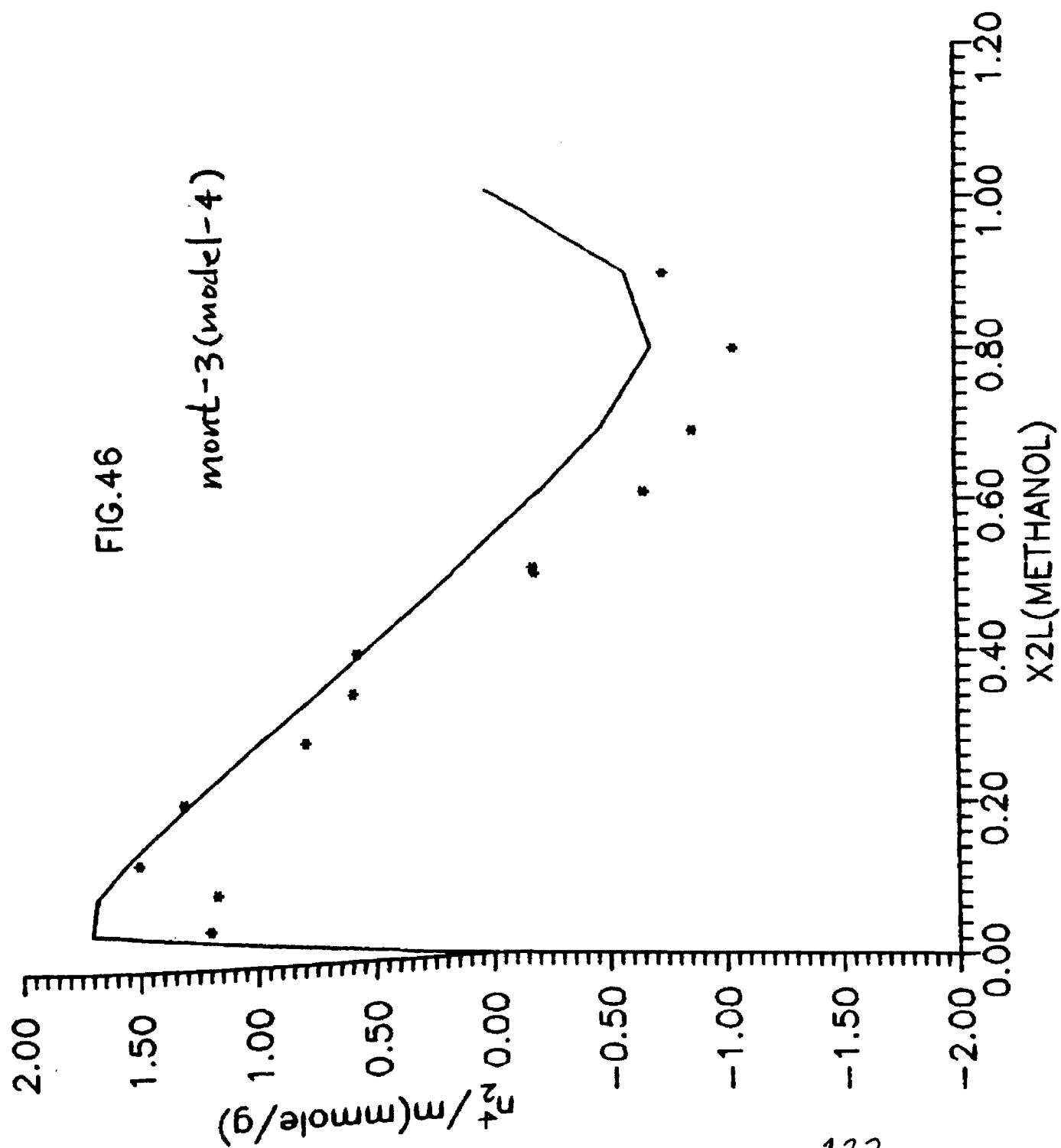


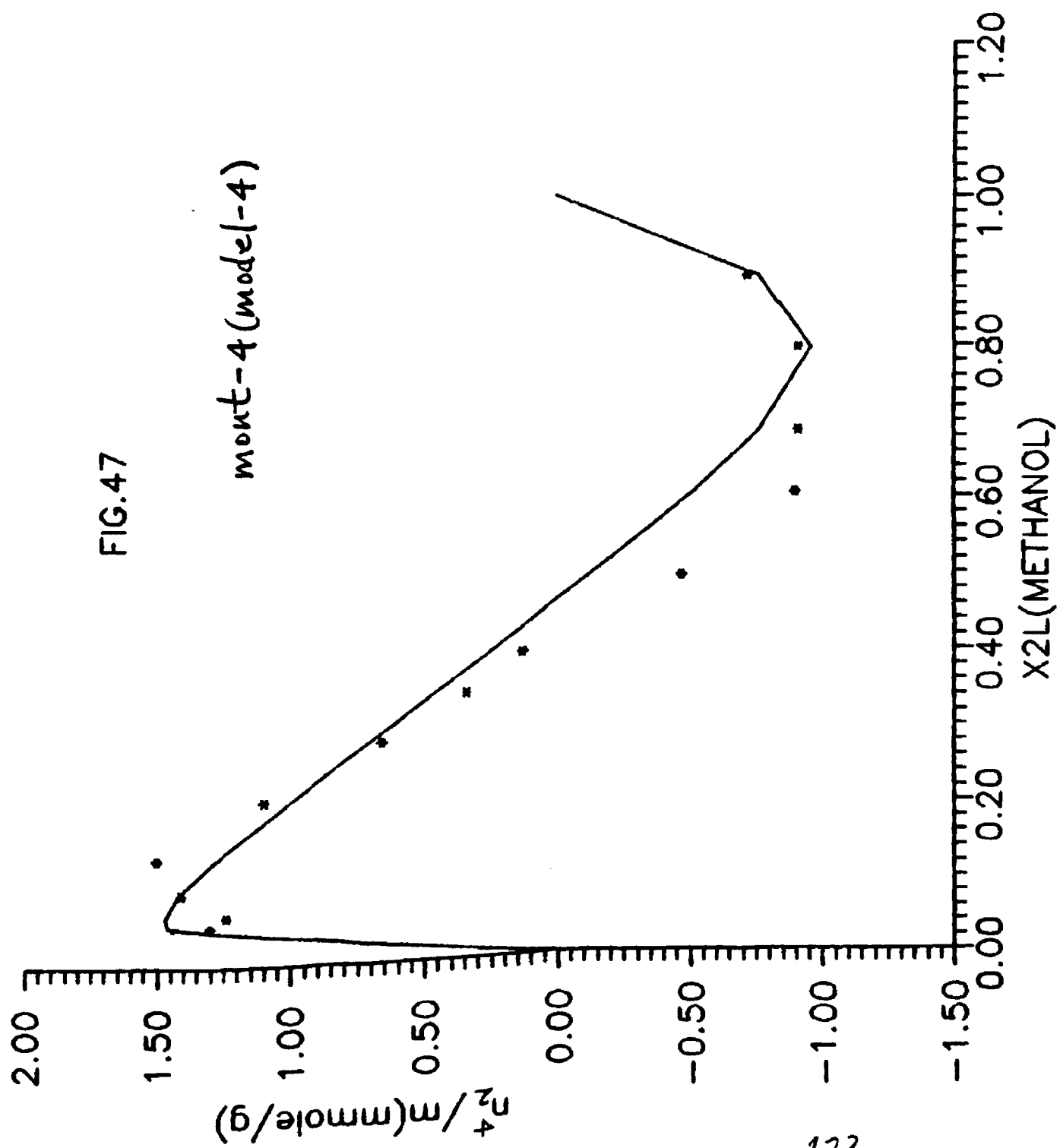




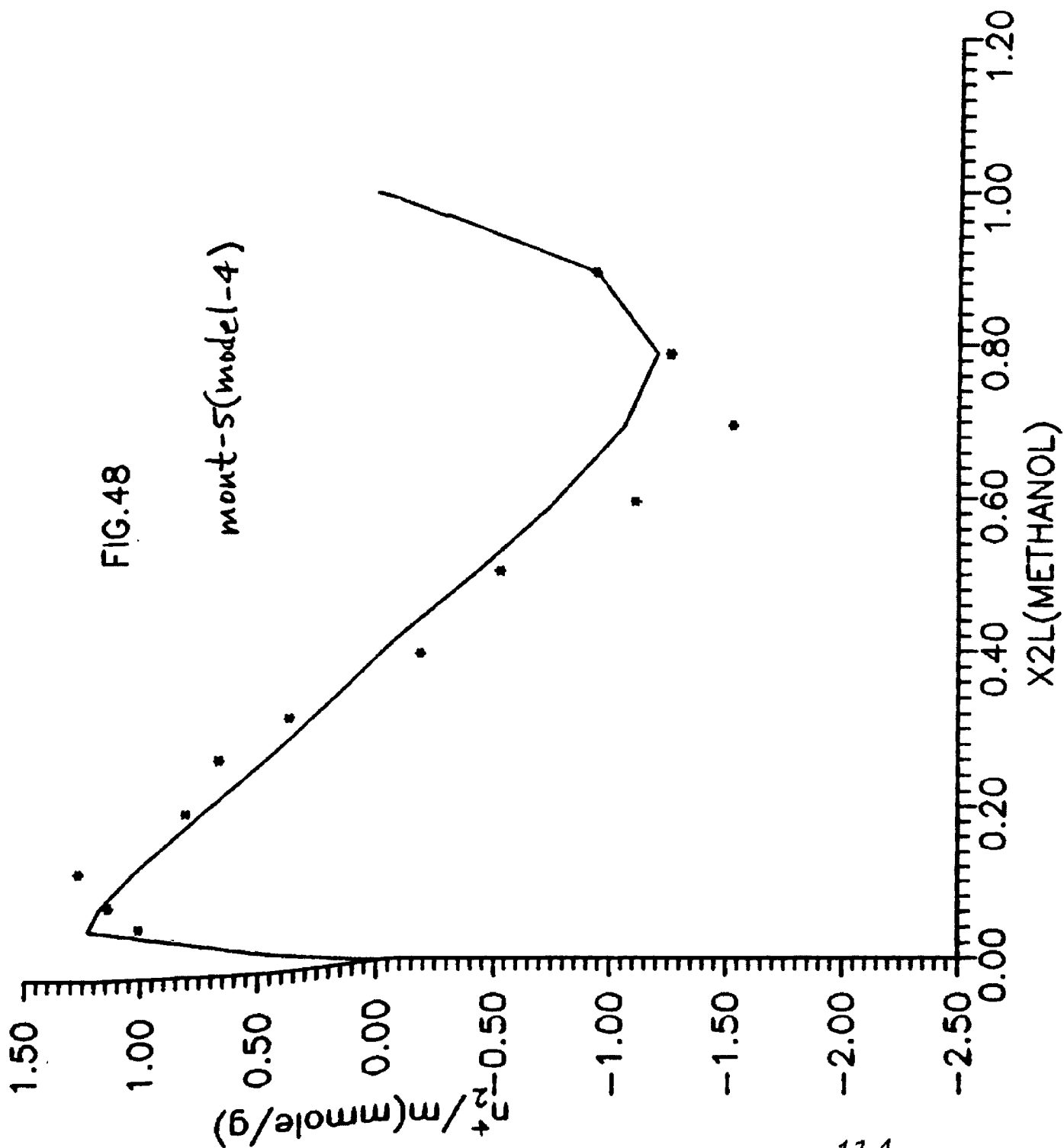


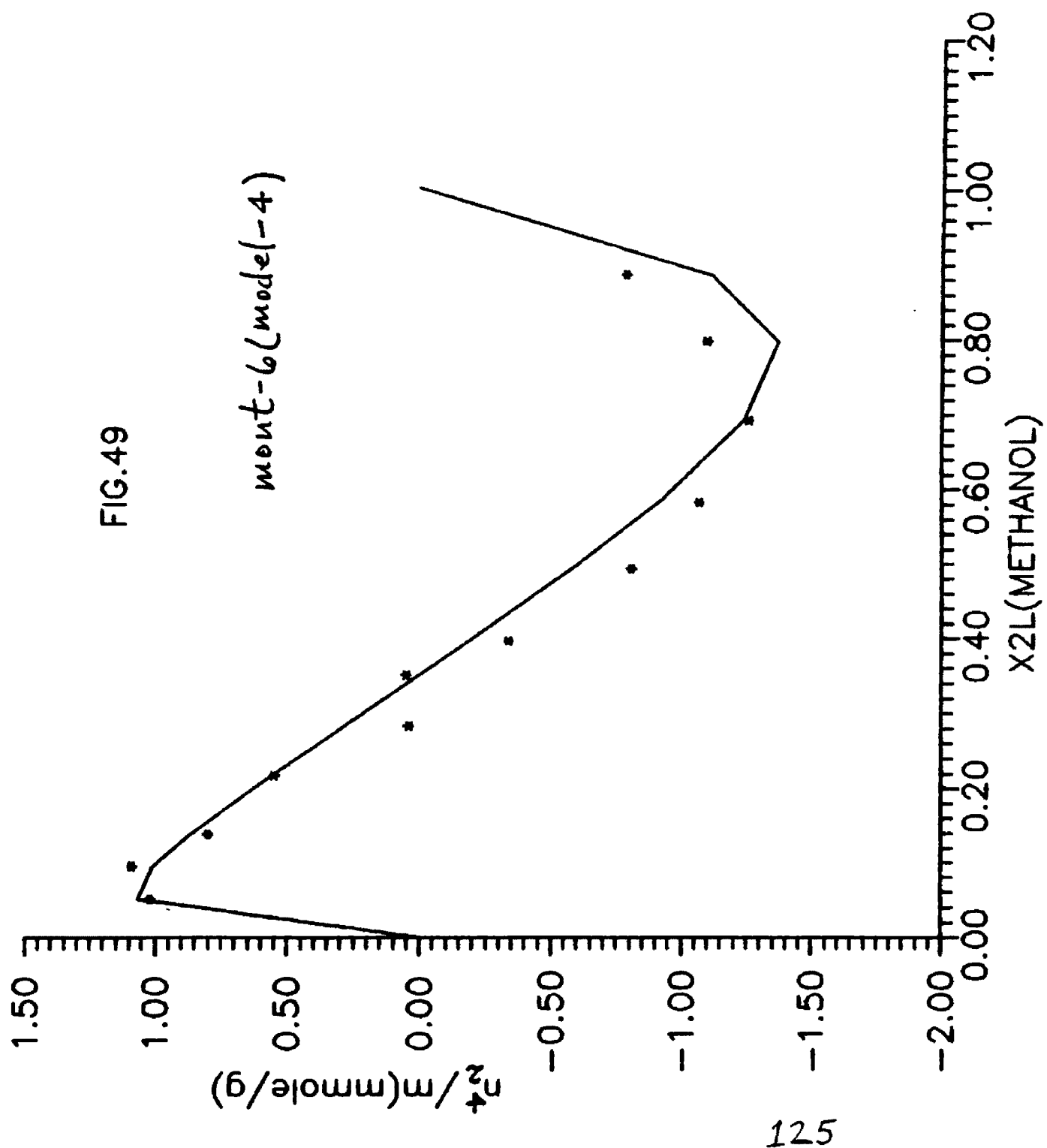
121

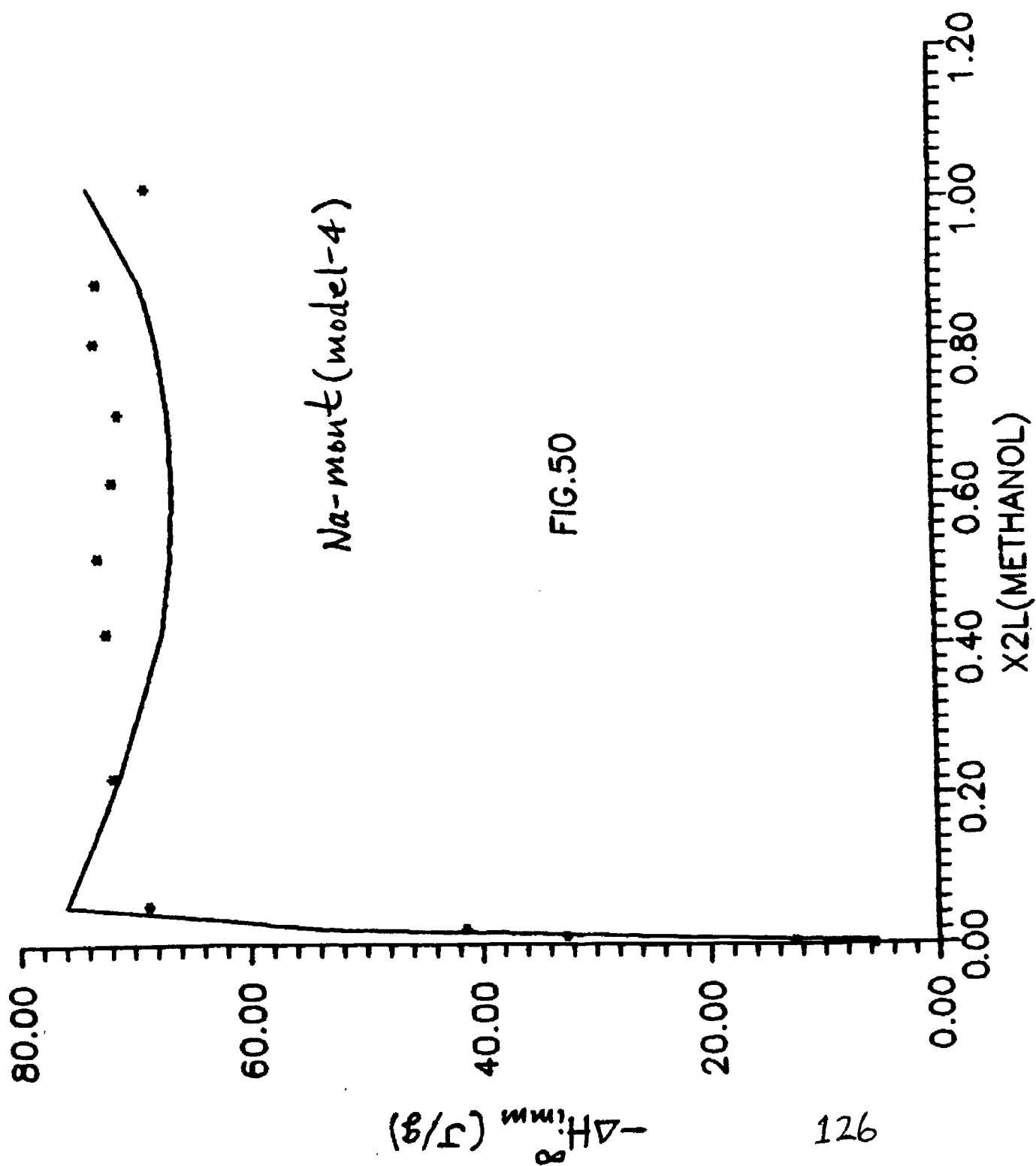


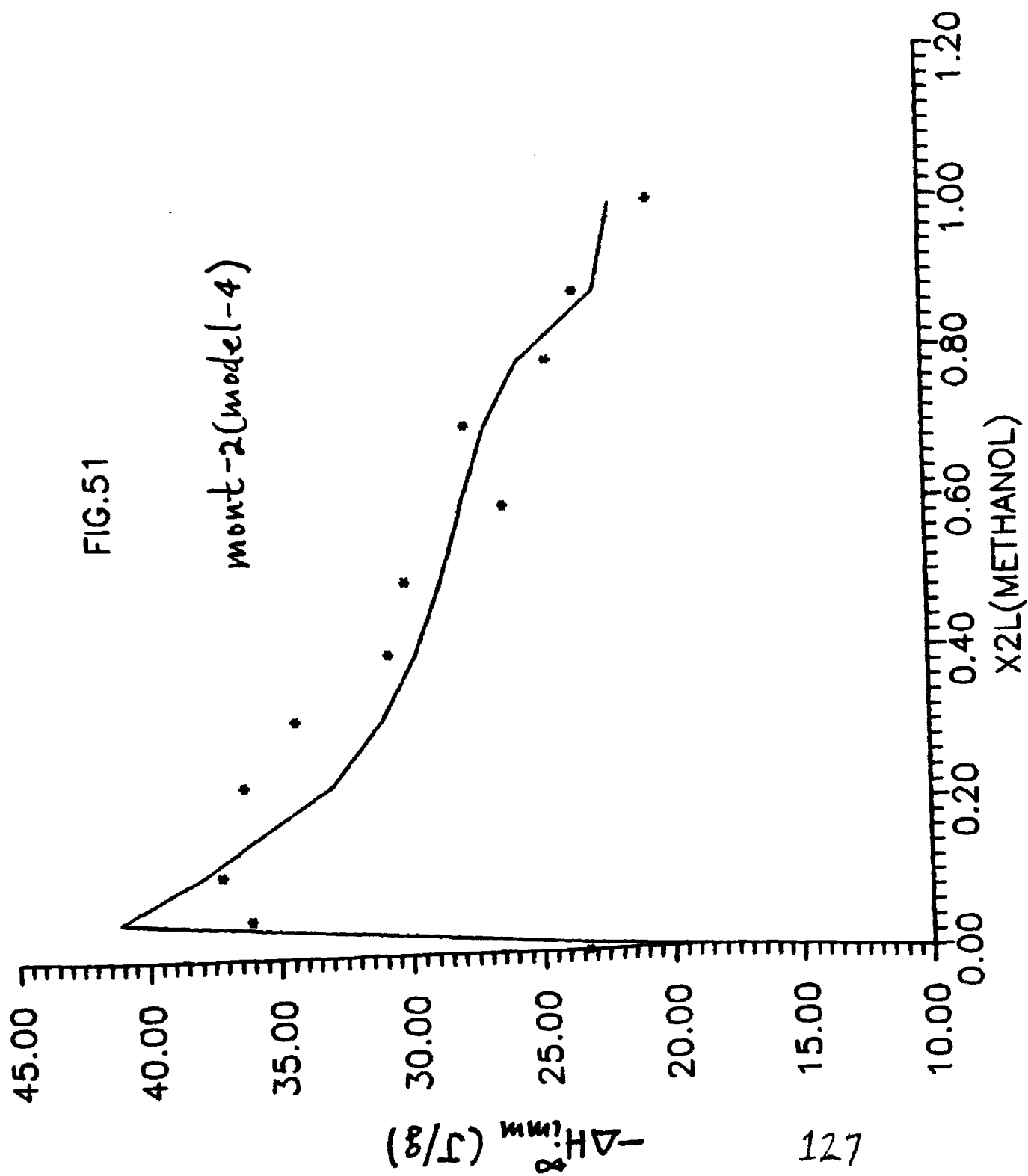


123







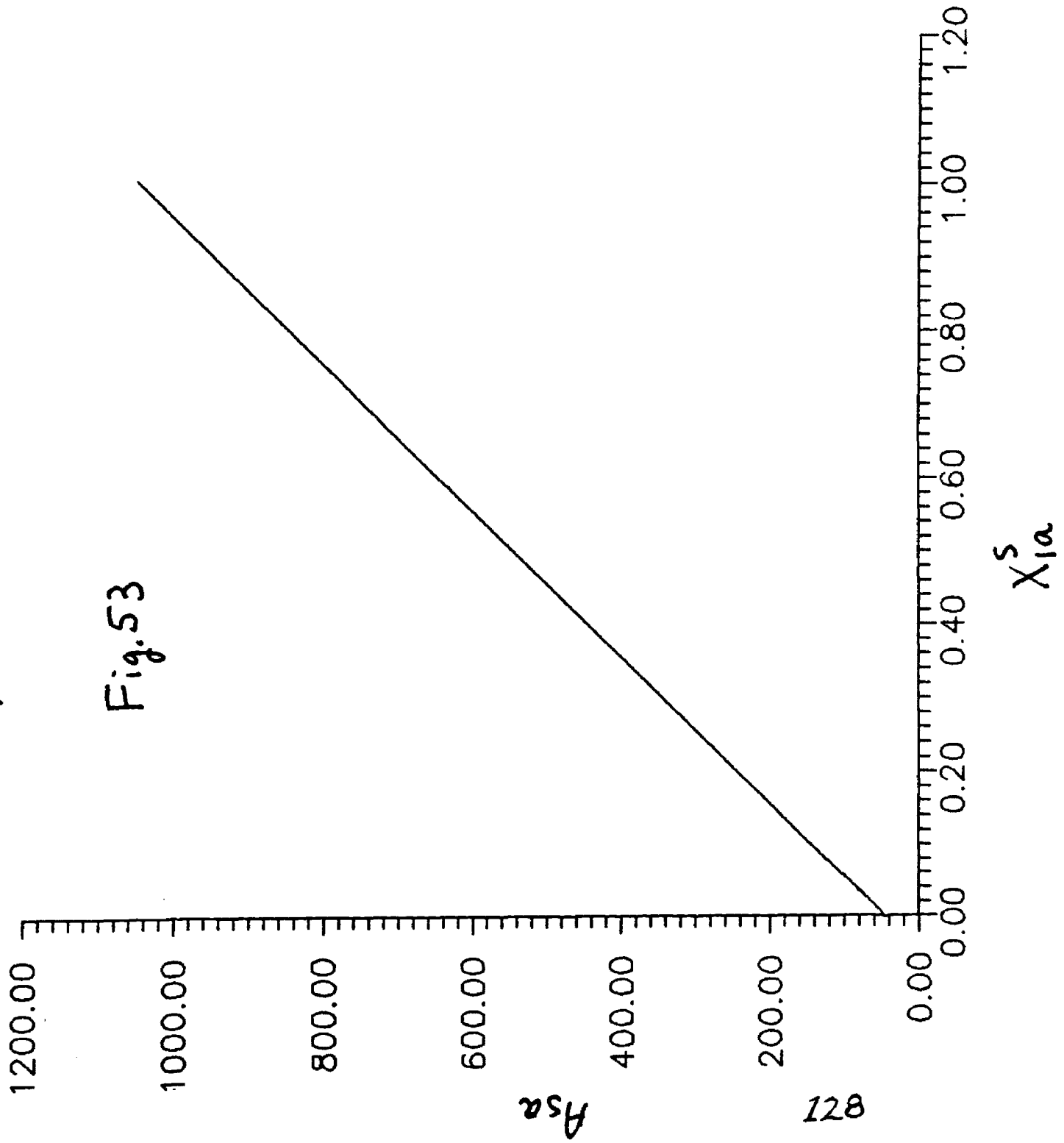


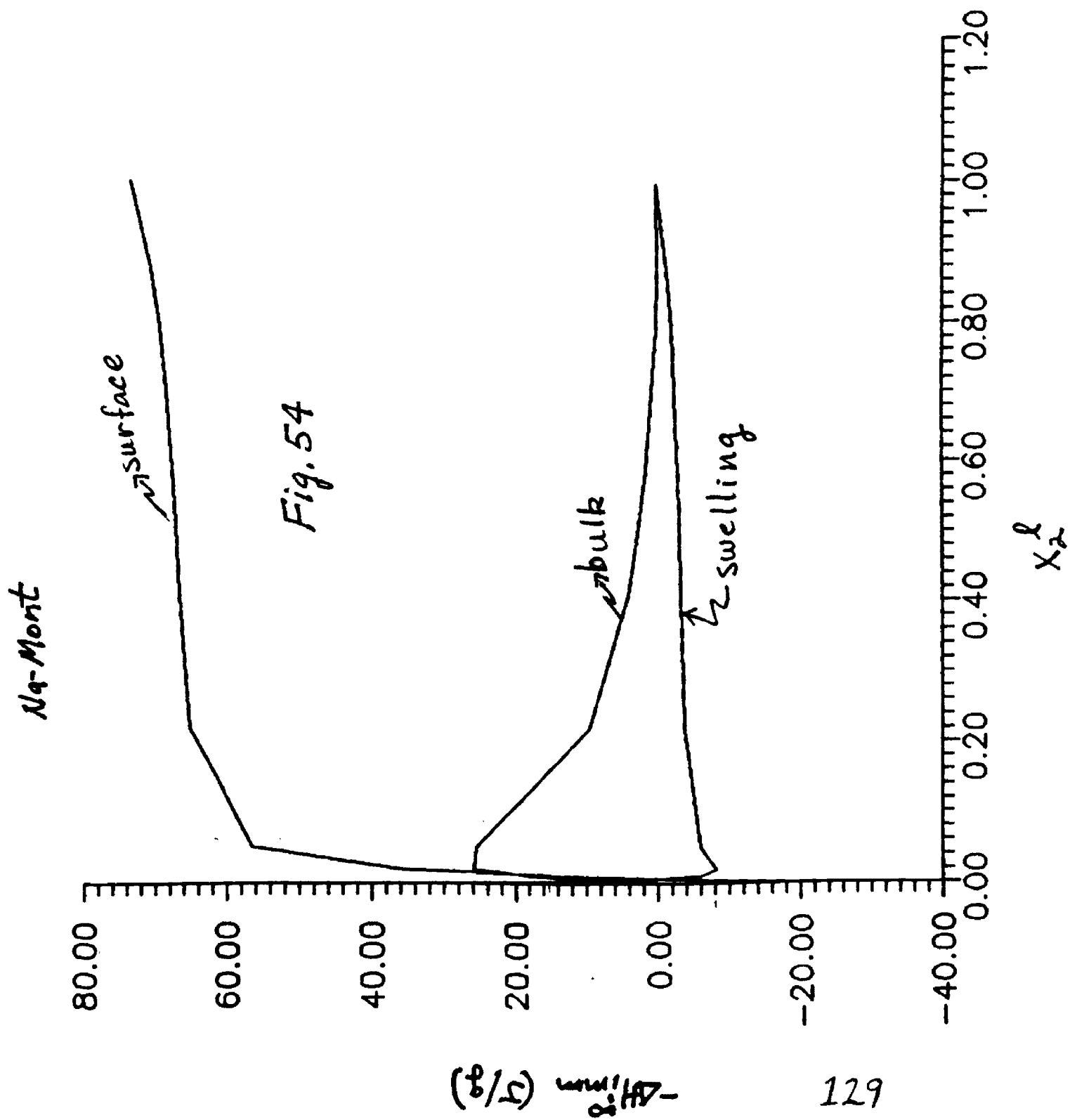
127



Mont-6

Fig. 53





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Mont-2

Fig. 55

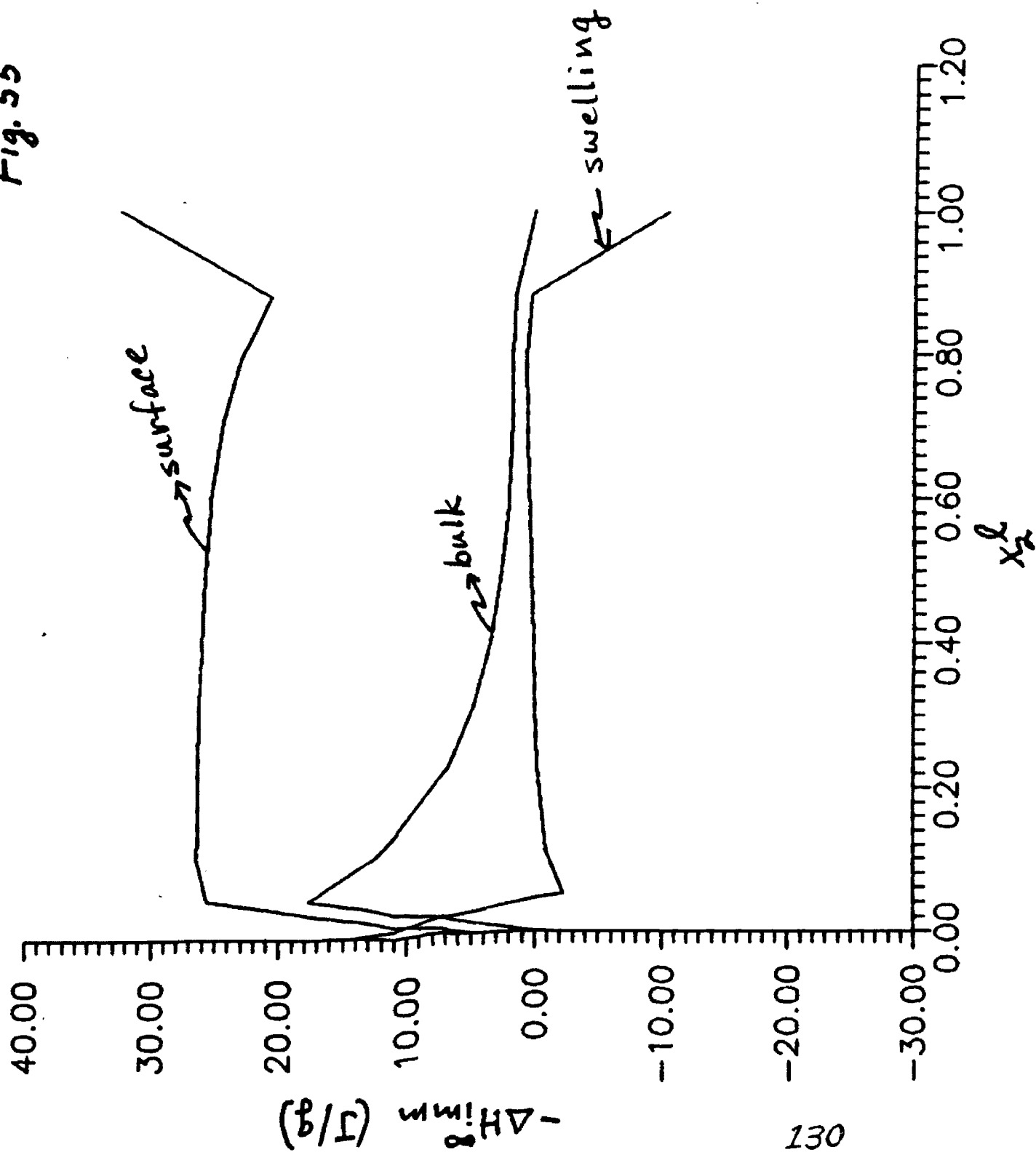
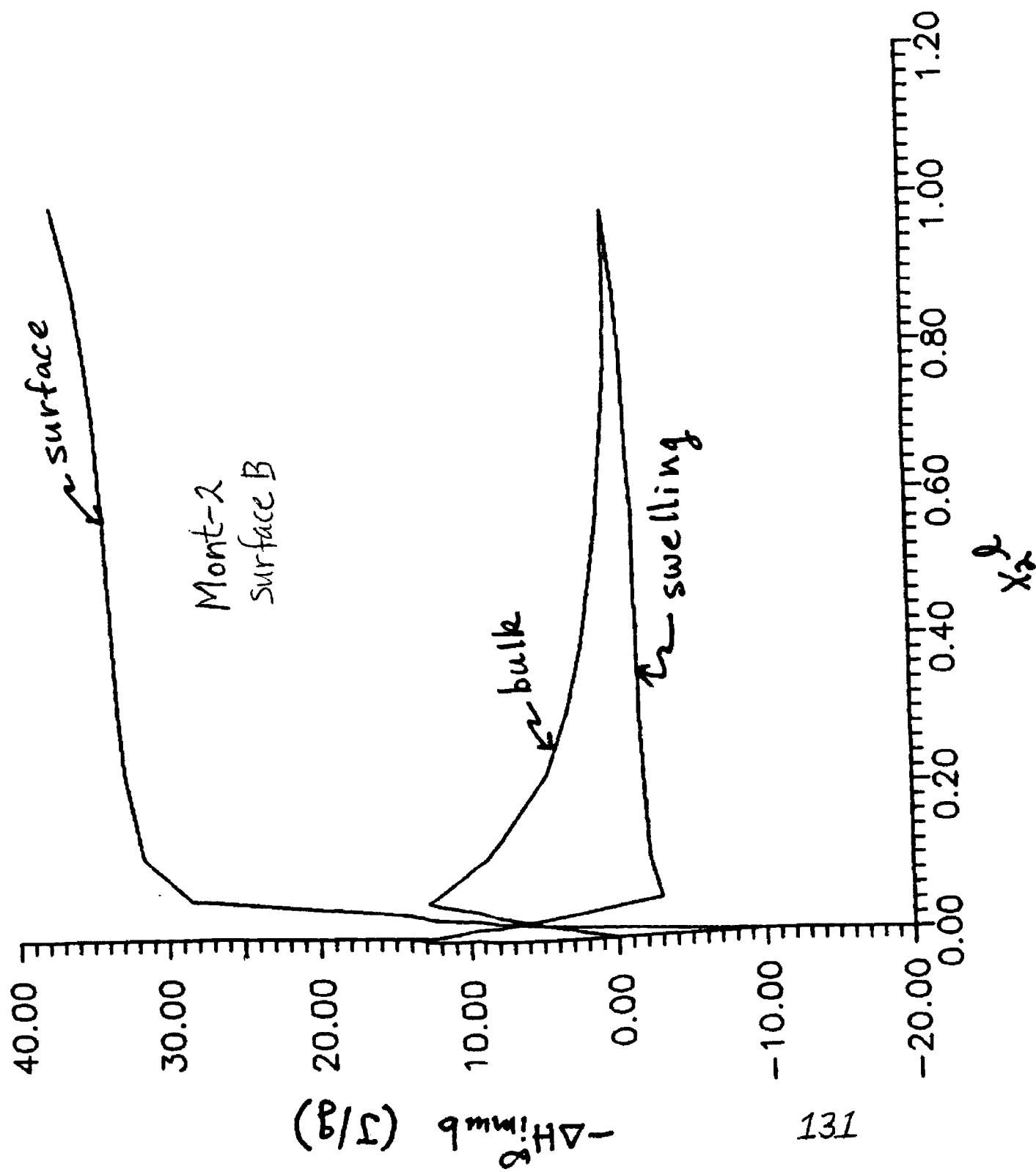
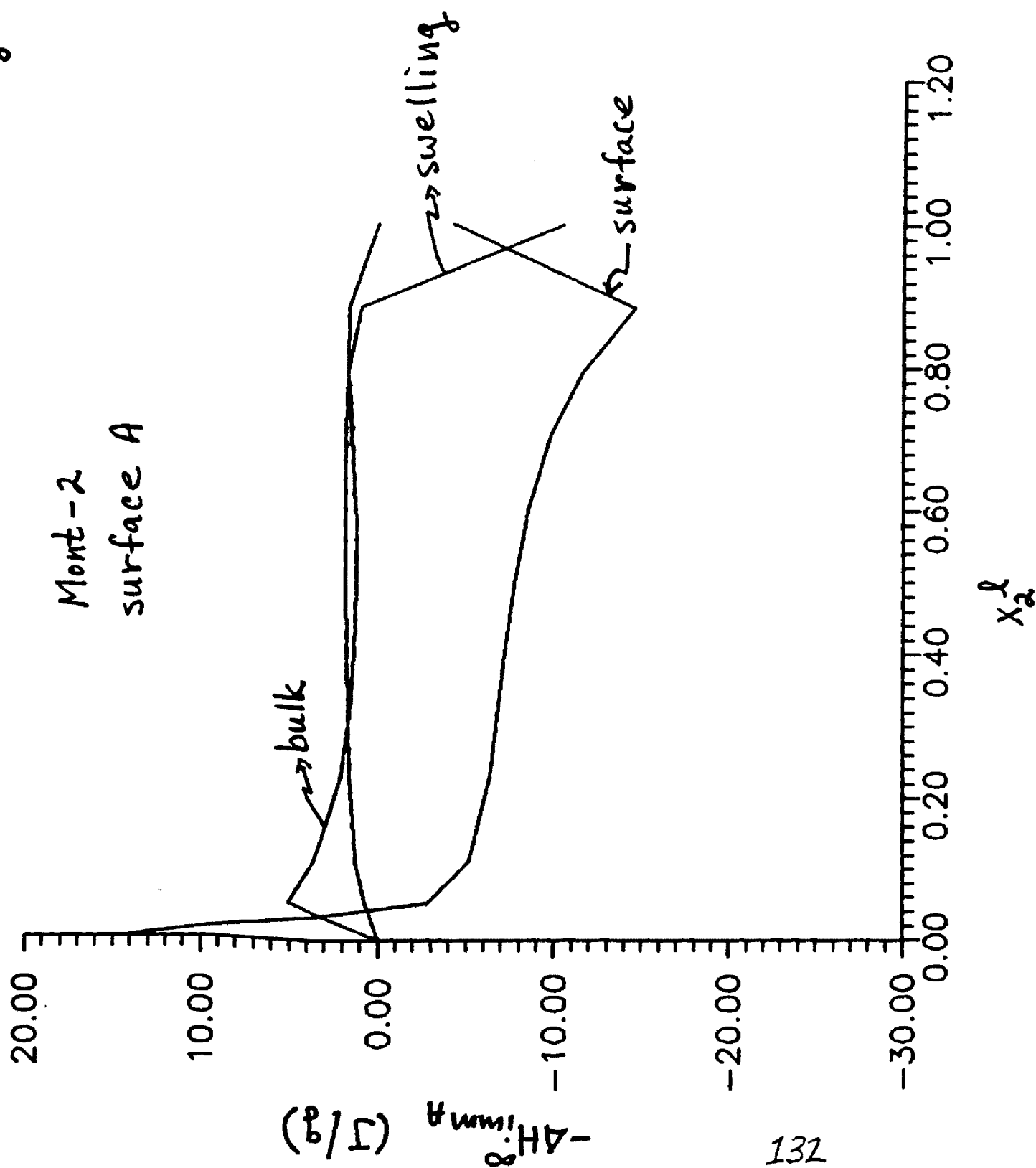


Fig. 5b



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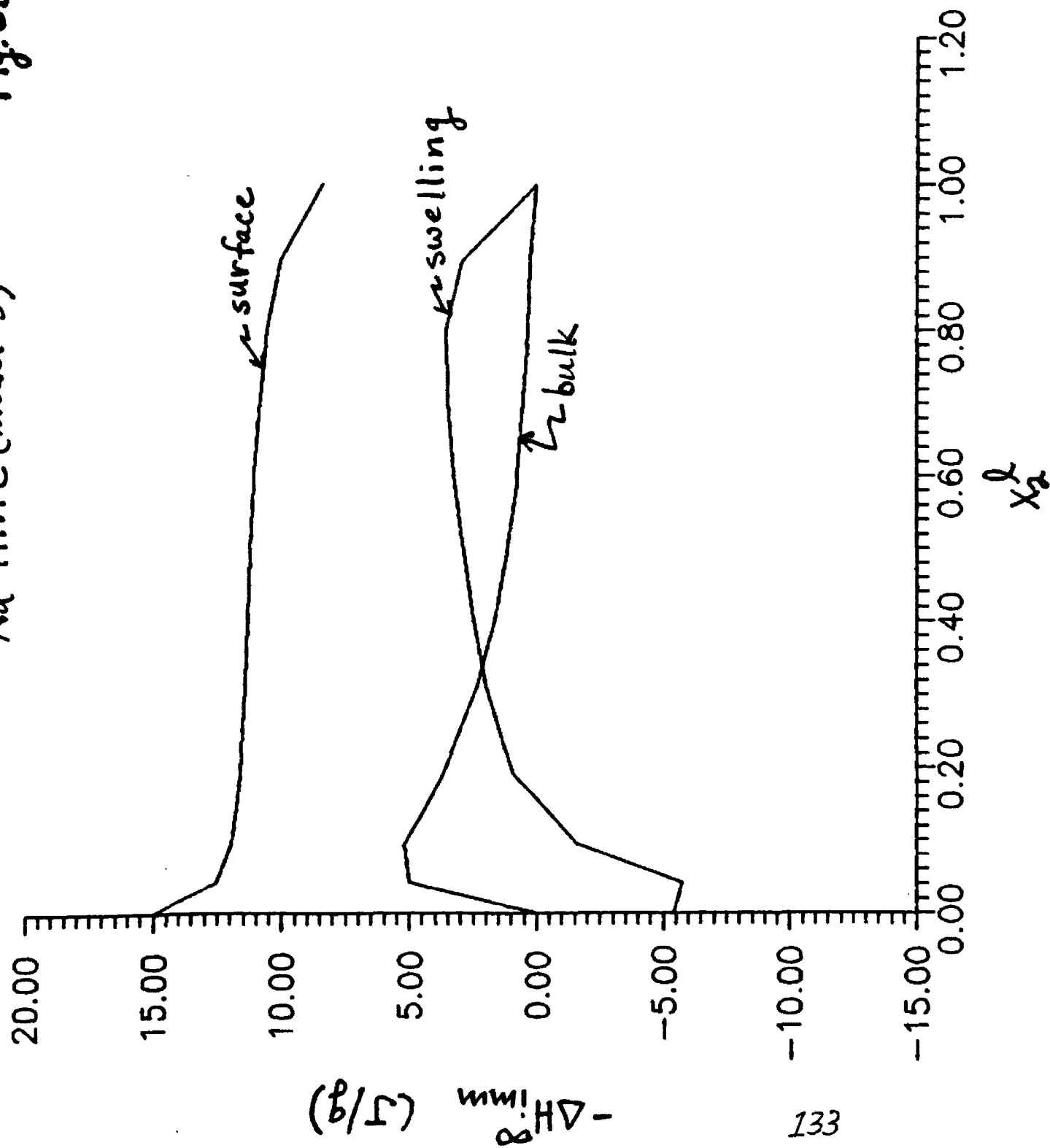
Fig. 57

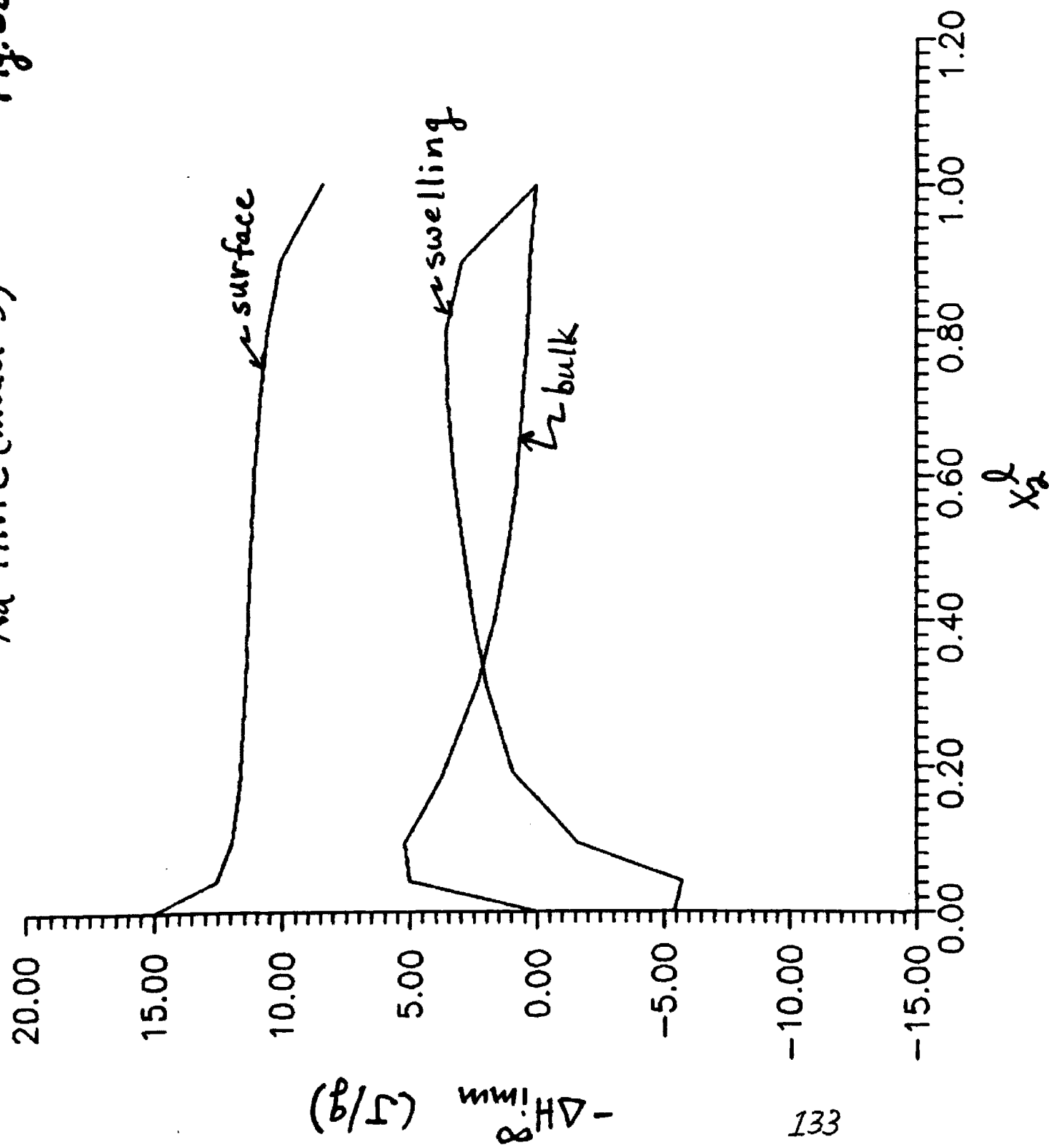


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Na<sup>+</sup> illite (model-3)

Fig. 58





illite-3 (model-3) Fig. 59

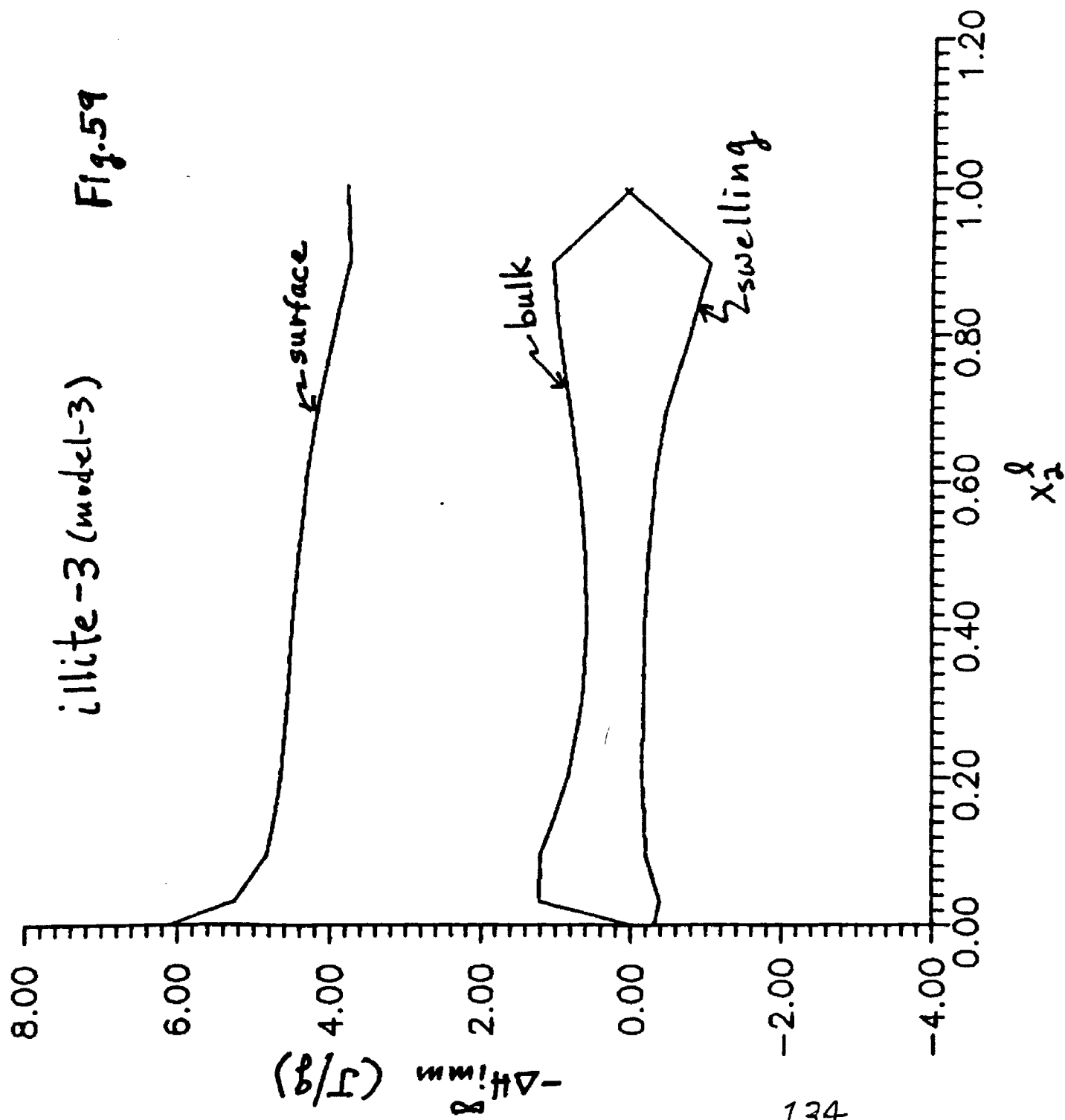




Fig. 60

illite-3 (model-3)

surface-b

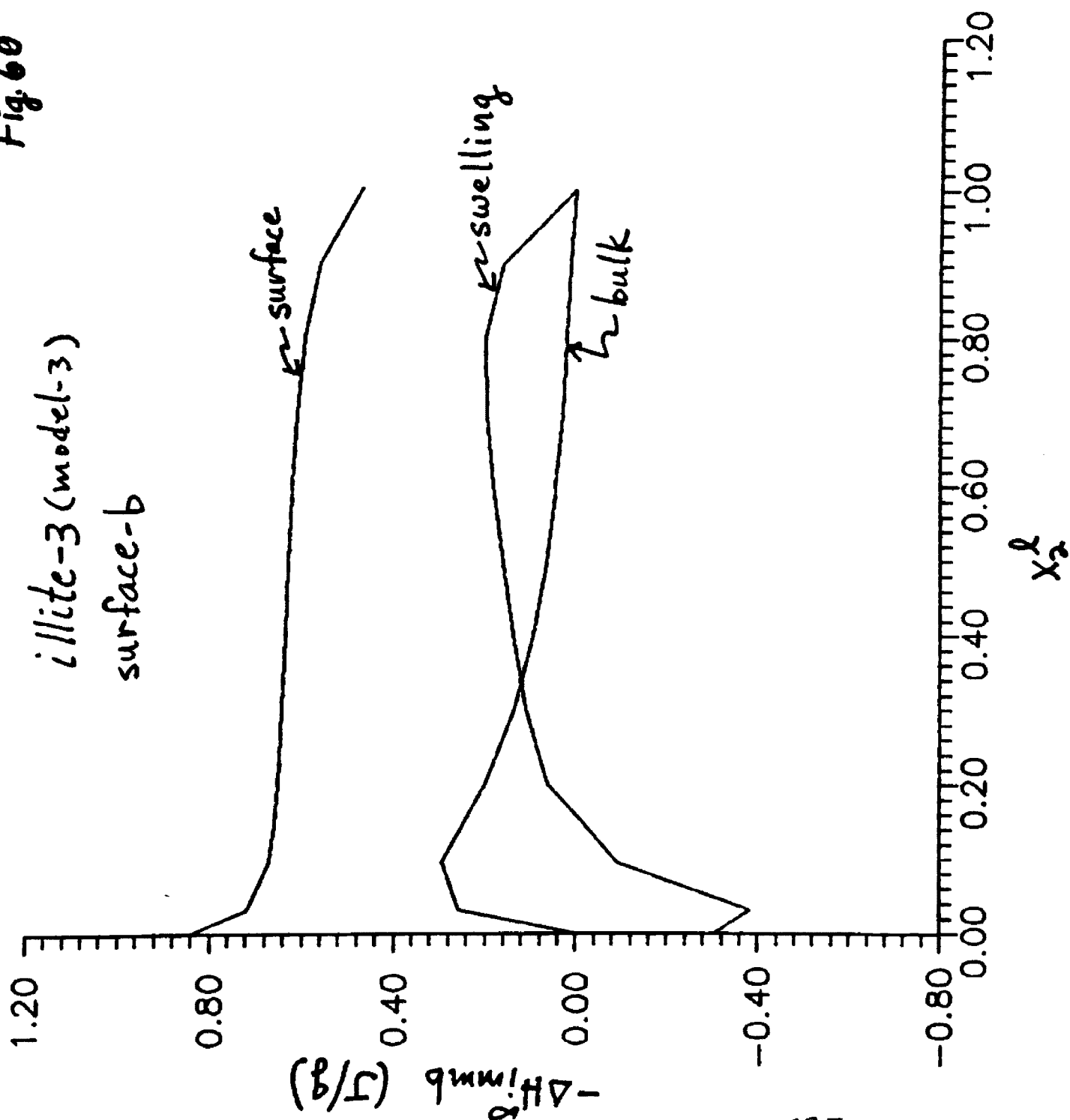
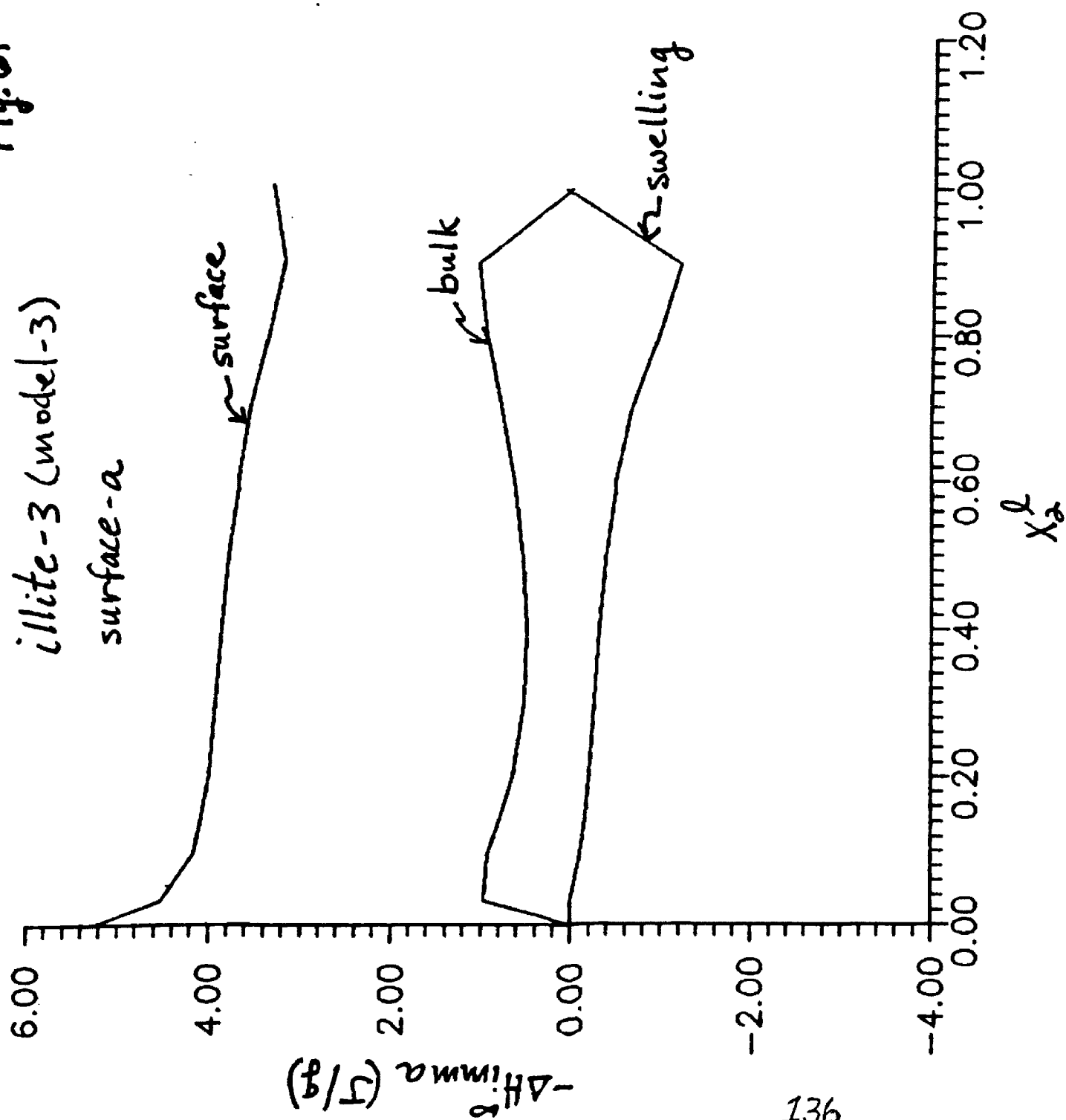


Fig. 61

illite-3 (model-3)

surface-a



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illite-2 (model-1)

Fig. 62

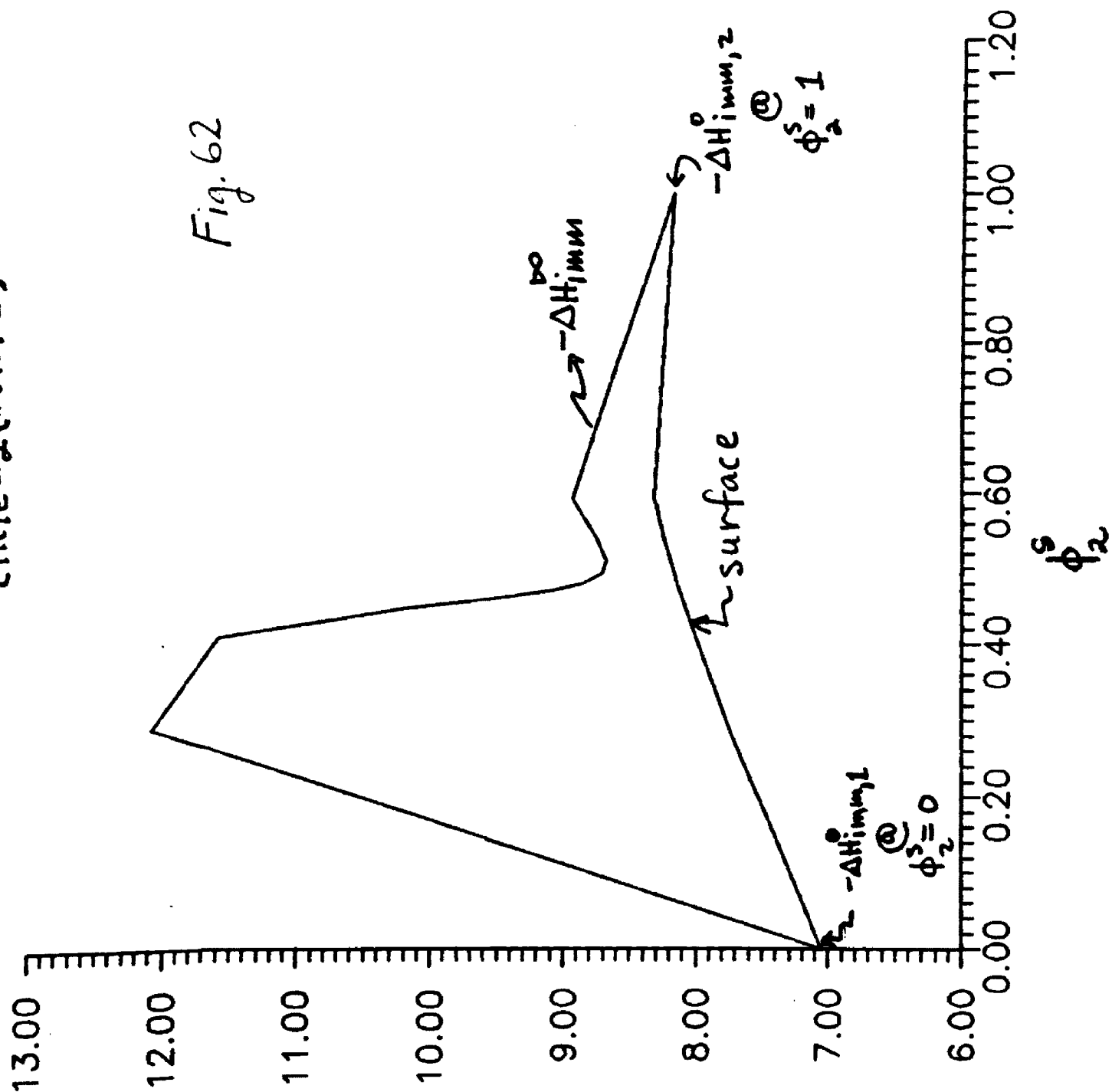
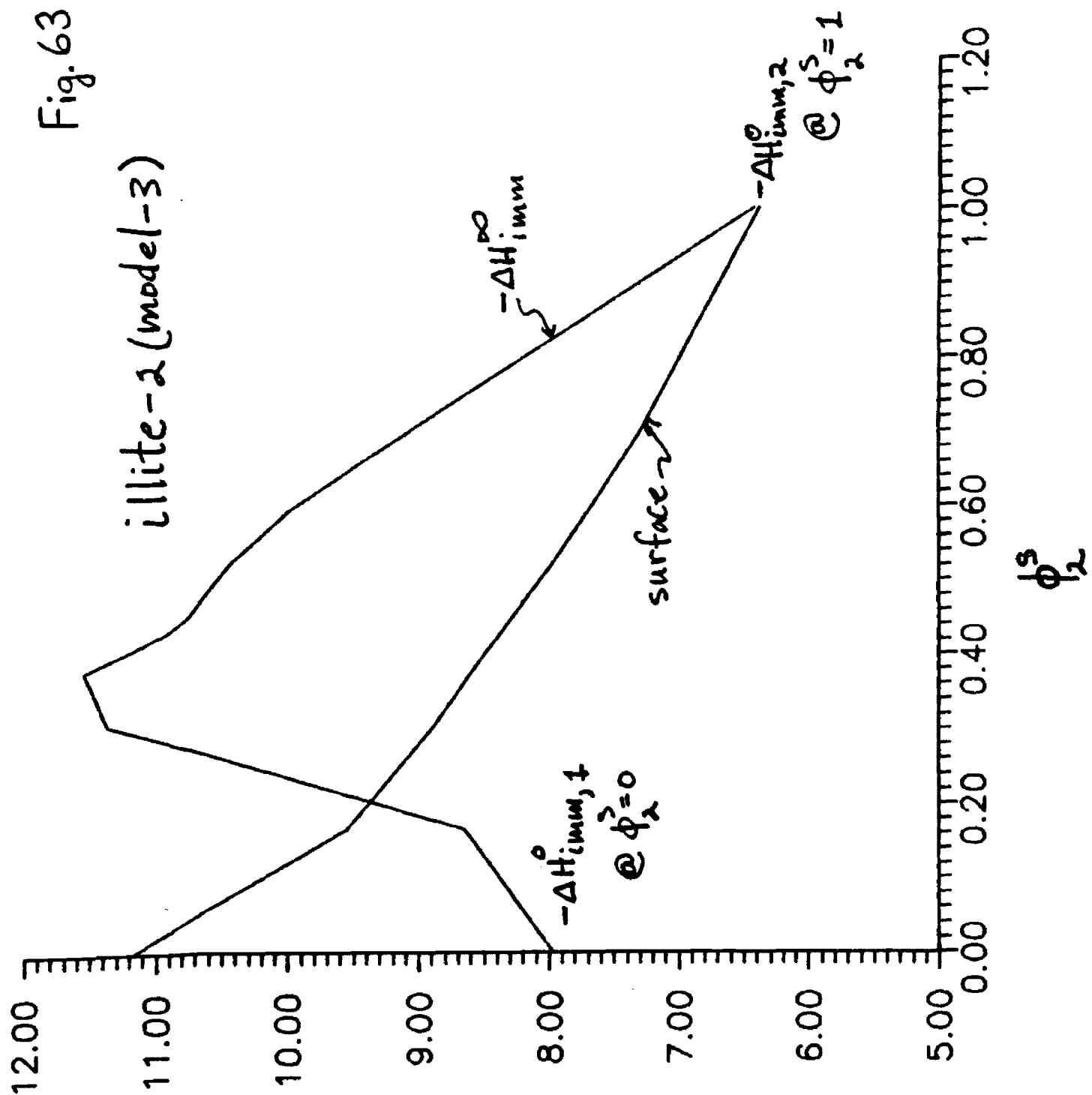
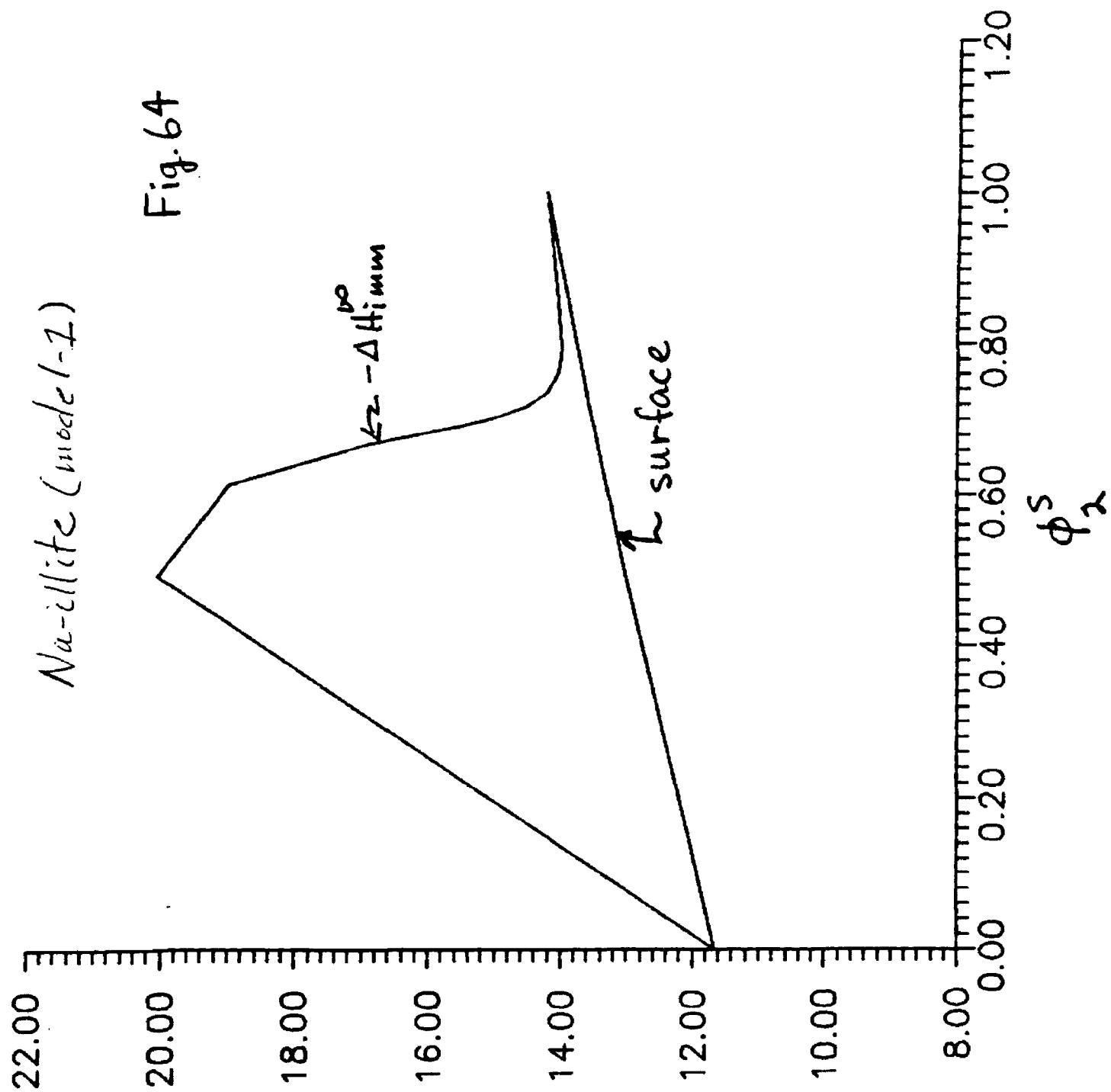


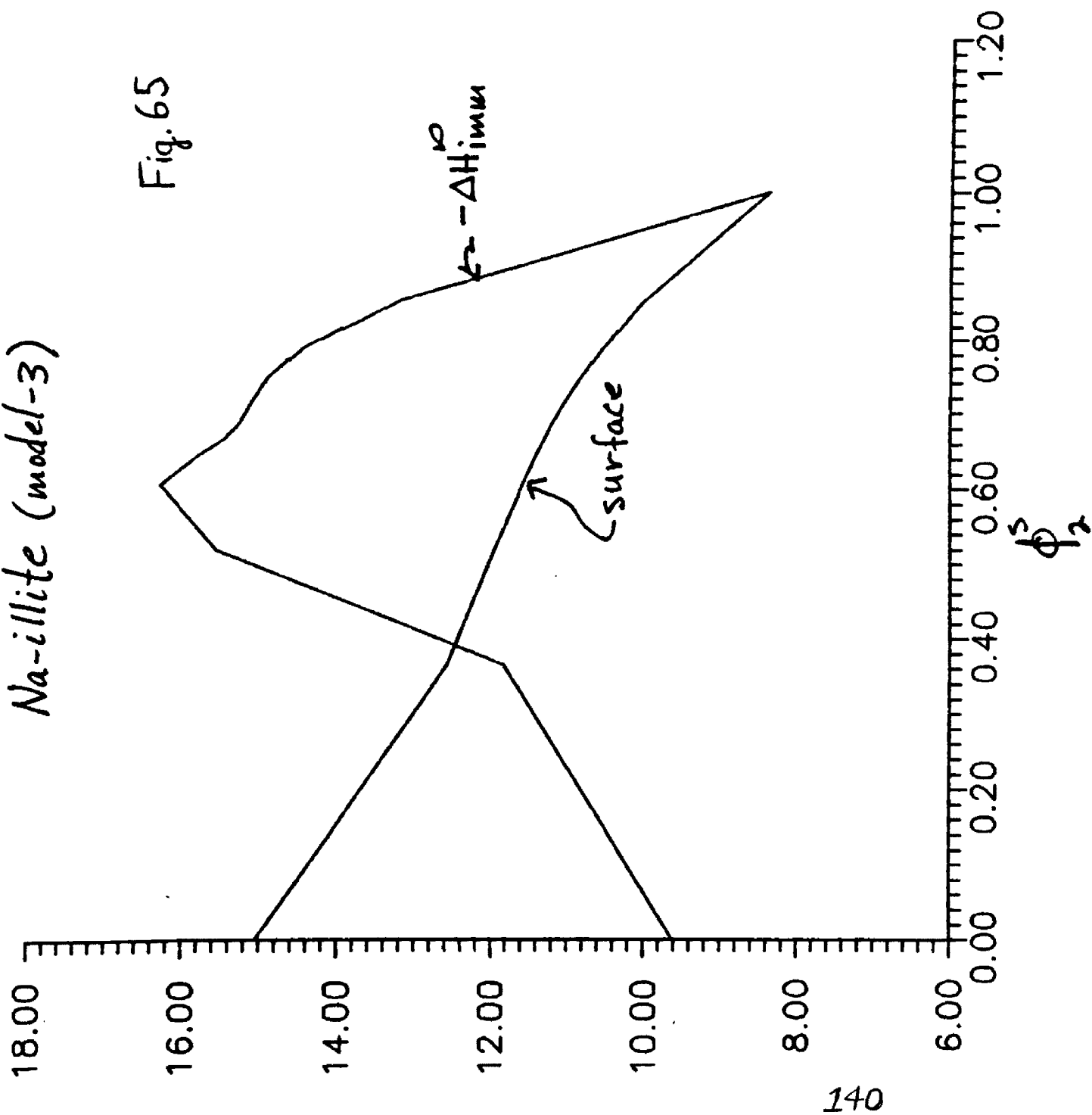
Fig. 63



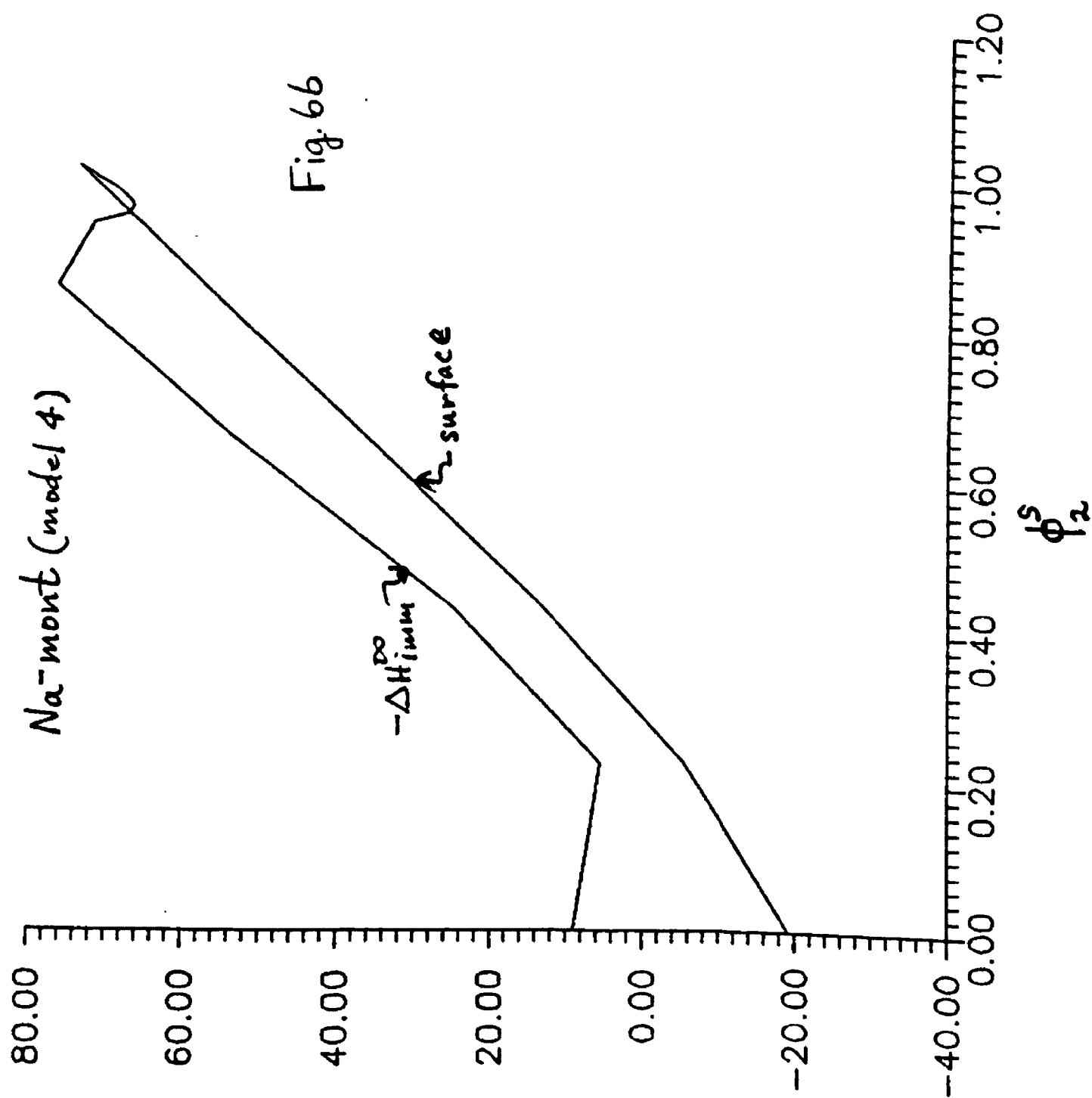


Na-illite (model-3)

Fig. 65

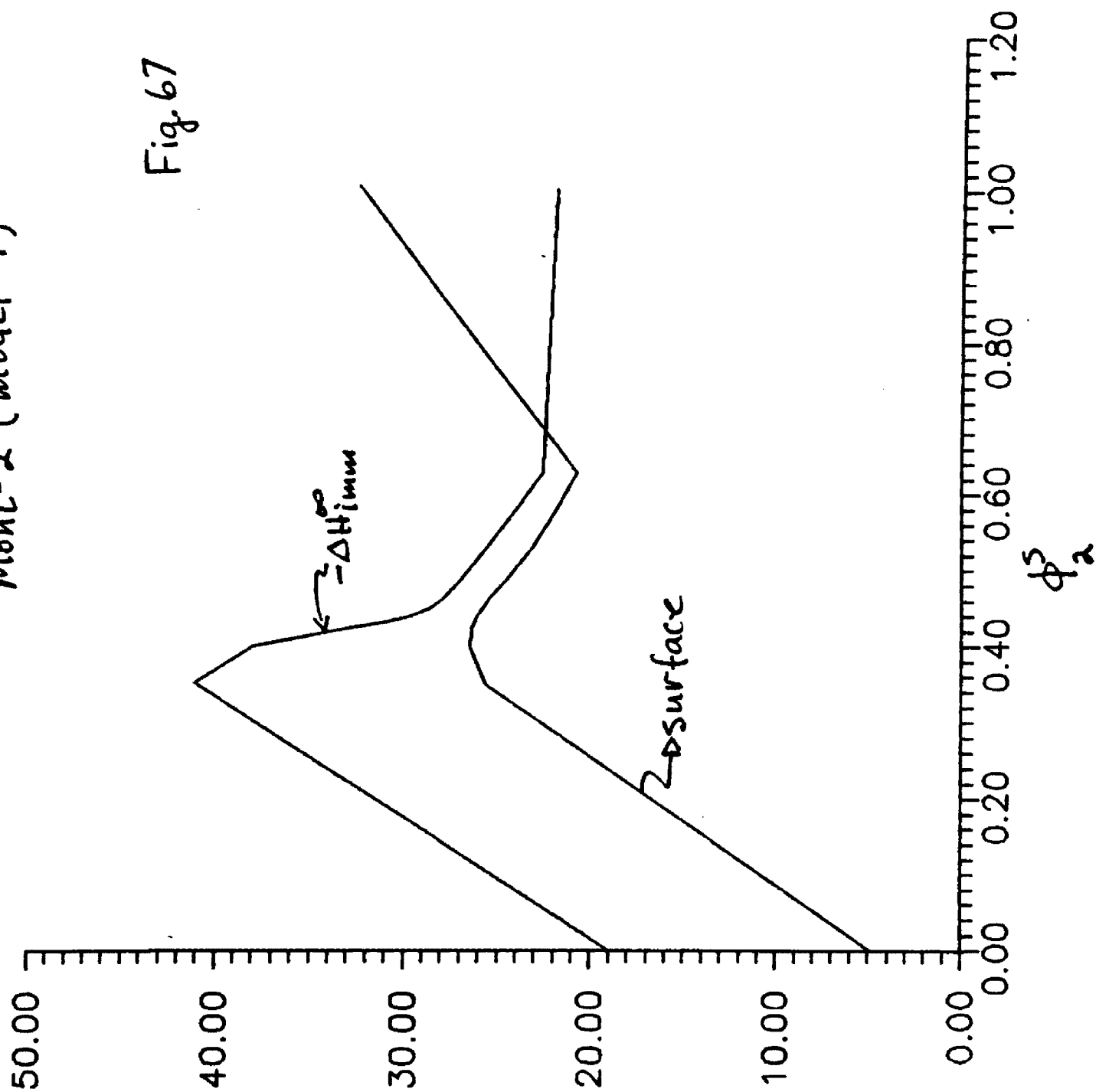


140



Mont-2 (model-4)

Fig. 67



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