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MULTIPLE EXTRACTION BY SLURRY SYSTEMS

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I. Introduction

Over the past several years, work has been done in these Laboratories to define a separation process which has the following properties:

1. It is particularly applicable to mixtures of liquid hydrocarbons.
2. The means of separation is a two-phase slurry of a shape-selective solid inclusion compound forming substance carried in a polar liquid solvent.
3. Equilibration of all phases is typically very rapid, so that continuous operation over more than one equilibrium separation stage is feasible.
4. Major contributions to the net separation arise from both components of the extracting slurry.

This technique, called slurry extraction, is capable of producing separations not otherwise easily done. At the same time, its properties place limits on the range of possible applications. As these capabilities and limitations are subjected to research, their better definition will serve to characterize the technique. Only in this way can slurry extraction take its proper place in the chemical engineering arsenal of unit operations.

The present writing will hopefully provide a basis for comparison of the general features of slurry extraction with those of other separation techniques. An illustrative case will be described in some detail.

The possibilities for industrial application of slurry extraction are numerous. No judgements as to economic viability will be presented here; the illustration has been chosen to describe the method, not as an industrially important separation.

Typical of the solid inclusion compounds central to slurry extraction are those of urea[1] and thiourea[2, 3]. Molecules which complex with urea are ordinarily long, such as n-paraffins of carbon number six or greater. Thiourea commonly forms inclusion compounds with substances of larger molecular cross-section, such as cyclohexane or 2,2-dimethylbutane. The normal crystalline structures of urea and thiourea show no voids capable of containing other molecular species. Inclusion of guest n-paraffin in the host urea crystal occurs by precipitation of guest and host simultaneously in a new crystal structure, wherein urea molecules form a matrix around the hydrocarbon chains. The presence of both guest and host appears to be essential for generation or even stability of this adduct structure. By contrast, the void spaces in such substances as molecular seives[4] are permanent, whether filled with guest species or not. The requirement for presence of the guest species implies an equilibrium limitation on the formation of this class of inclusion compounds. This "cleanup limit" will be discussed in Section III, to follow. A third class of shape-selective systems is that of true solution, wherein host, guest, and inclusion compound may all remain dissolved. Shape-selective of this latter type is quite unusual outside of biological systems. The complexes of interest in slurry extraction are therefore intermediate in solubility between totally dissolved systems and permanent solids (seives). They are cycled between solution and solid in the course of selective compound formation. The question of how to utilize such complexes

efficiently on an industrial scale led to the development of slurry extraction. The technique offers more to separations technology than the properties of the solid alone, as already pointed out.

II. Historical Background

Chlorine hydrate, discovered in 1811 by Davy,[5] was the first solid inclusion compound studied; although it was not correctly identified as such at the time. Because such solids depend for stability on a match in size and shape between a guest molecule (chlorine in this case) and a hole in the matrix of crystalline host (e.g., water), the molar ratio of guest to host need not be a small whole number. Considerable scientific effort was often spent in erroneously trying to force a fit to the law of simple multiple proportions;[6, 7] this often delayed a true understanding of such substances. The actual molar composition of chlorine hydrate is 7.27 ± 0.17 $H_2O \cdot Cl_2$, as established by Allen in 1959.[8]

Since 1940, when urea inclusion compounds were discovered, an inexpensive host substance for inclusion compound formation from a wide range of guest species has been available. From the viewpoint of laboratory investigations, urea separations are almost ideal: the selectivity is high, complexes and host are easily filtered solids and ambient temperature and pressure operations permit study of reasonably stable complexes. Industrial-scale processing with urea normally centers on extraction of long-chain linear paraffins from liquid hydrocarbon streams, wherein the paraffins are of value to the chemicals industry and the depleted feedstocks are improved in value for such uses as fuels or lubricating oils. The transition from simple laboratory practice to plant operations in this case is not at all straightforward, for the following reasons:

1. Distillation has historically been the key separations process in the petroleum industry. Simple application of heat to complex mixtures leads to continuous operation,

with hardware no more complicated than fractionation towers. In contrast, urea complexing is based on precipitation of a solid phase. The operational difficulties of nucleation, precipitation, washing, filtering, and recycling of any solid, on a continuous basis, on the basis of thousands of barrels of throughput per day, are formidable.

2. Perfectly dry urea and liquid normal paraffins, although overwhelmingly favored to produce inclusion complex from equilibrium considerations, may do so at an imperceptible rate unless some polar liquid is present as an "activator." The probable mechanism of activation is solution of urea and hydrocarbon in the liquid followed by re-precipitation of adduct. If only a trace of activator solvent is present, there may be a correspondingly slow rate of equilibrium of the solid urea charge. If an activator is chosen which has little tendency to dissolve hydrocarbon, the mass transfer of hydrocarbon may limit the rate. If a major fraction of activator is used, the system must incorporate more processing to recover it. A balance between these factors must be achieved in any industrial situation; some highly sophisticated proposals have been made.
3. While large needles of solid inclusion compound are desirable for laboratory filtration, they may spell disaster for industrial scale operations. Unless special provisions are made, the adduct needles may interlace to plug process equipment. Filtering or centrifugation may be complicated by the tendency of complex to entrain liquid hydrocarbon in a buttery mass.
4. It is true that urea and thiourea complexes are highly selective, but they are not infinitely so. A batch precipitation of urea-linear paraffin adduct from a mixture

of hydrocarbons will not produce 100% product purity of extract. One reason for this is the inevitable presence of some occluded liquid on the solid particles. Another problem is co-precipitation of normally non-adducting impurities in the inclusion compound structure itself.[9] This phenomenon is observed in thiourea adduction as well. Product purity requirements may dictate a second cycle of adduct precipitation.

Mention is made in passing of another fact of life in the chemicals processing industry which has affected the commercialization of urea processing: the ideal separation process yields two desirable products, not one. The demand for linear paraffins has historically been orders of magnitude less than that for the large-volume fuels which are improved in quality by the removal of linear paraffins. Thus, it is possible to remove low-octane linear molecules from motor fuels, but the absence of a good use for the linear paraffins, the loss in volume caused by their removal, and the existence of inexpensive alternatives to the separation such as addition of lead derivatives or conversion processes (reforming, isomerization) have produced an environment generally unfavorable to urea process development for this application.

In spite of the above restrictions, there are a number of operational urea separations processes on the industrial scene at present, and a much larger number are described in the patent literature. Many of these are cited in a recent publication by the author.[10] The present discussion will cover selected processes in terms of various approaches to the major problems, as a background for description of slurry extraction.

Urea solution in water, saturated at 70° C, is mixed with feed hydrocarbon and dichloromethane oil solvent at 40° C in the process of Deutsche Erdol A.G. (Edeleanu process).[11] Dichloromethane boils at 41° C; its vaporization provides auto-refrigeration while its presence lowers the oil viscosity. The system is mixed

so as to agglomerate urea adduct, wet by the water, into large lumps which are separated from raffinate by simple screening. Holdup of liquid with the solid is minimized. The extract purity may be greatly improved by "re-pulping," i.e., dispersing the adduct lumps in a wash solvent. A second agglomeration and screening follows. This process has been operated commercially since 1955.

Reduction of the activator proportion directionally leads toward maximum extract purity and minimum equilibration rates. Sonneborn Sons,[12] Mendeleev Institute,[13] and Nippon Mining[14] all utilize this "solid urea" approach. When the activator added is only about 1-2% of the feed mixture, the conventional filtration of adduct crystals is easier, since activator substances tend to wet the crystals and promote their physical association. The Edeleanu system takes advantage of this, in radically different filtering operations.

One approach to the problem of adduct handling is to distribute urea on a solid support. The resulting mixture is then used in a fixed bed scheme.[15, 16, 17] Operationally, the urea must change its crystal structure completely each time it cycles between empty and loaded conditions.[18] This suggests that occasional redistribution of urea would be required. Provision is made for this in the process description.

When the proportion of polar solvent in the system becomes large enough to carry the solid as a moving fluid mixture through processing steps, some of the characteristics of slurry extraction become evident. Fetterly described equilibration over, and subsequent separation of, three phases: solid complex, a solution of aromatics from the feed mixture in a solvent which is a nonsolvent for the other components of the charge, and depleted feed mixture hydrocarbons.[19]

Operation over two liquid phases and a solid complex phase brings up the question of relative densities. For wax extraction from a kerosine mixture, conditions have been described which

lead to the density series urea >reject oil > complex $\approx$ solvent.[20-23] Light aliphatic alcohols can be used as solvents.

A process of Shell uses water-methanol solvent with urea. Depleted hydrocarbon liquid evidently forms the top, or lightest, phase in this case.[24] Urea is activated by methanol, while the presence of water keeps the holdup of dissolved hydrocarbons to a minimum.

Champagnat and Vernet have produced a series of inventions concerning mixed slurry solvents for urea processing.[25] Water is evidently a major solvent constituent in their systems. As in the Shell process, it lowers hydrocarbon solubility, but the additional properties which it introduces are instructive to consider. Reference has already been made to possible lowering of the adduct equilibration rate. Another rate effect is seen when small droplets of raffinate show reluctance to break out of suspension in the slurry. These investigators found means to produce quite small adduct crystals so as to reduce entrainment of raffinate by the needles of solid. Additional suspension-breaking operations include dilution with aqueous methanol, an unusual vibration-decantation, and stirring with a stream of gas bubbles. Mild agitation of the slurry has been proposed by Keller,[26] after vigorous mixing for equilibration, to separate raffinate from slurry.

Investigators at Phillips have described the use of sulfolane as a slurry solvent.[27] This system appears to facilitate smooth raffinate-slurry separation, and allows recovery of aromatics extractable by sulfolane as well as linear paraffins complexed by urea.

In general, the operational techniques proposed for urea complexing are readily extended to separations using thiourea. Thiourea systems appear to show no systematic relationship between complex stability and increasing molecular weight of guest substance, however, as observed for urea complexing.[28,29]

The literature of inclusion compounds has been periodically reviewed.[6, 10, 30-42] Many of the systems reported, in addition to urea and thiourea, could be cast into separation schemes such as those just discussed, or could be utilized in slurry extraction processing as it will be described.

III. Process Features

A. Phase Separation

In order to ensure the existence of all phases upon which slurry extraction depends, the system must contain the following elements:

1. A relatively nonpolar liquid feed mixture, such as a hydrocarbon stream.
2. A relatively polar solid complexing agent.
3. A relatively polar solvent.

Mixtures of the solvent and components of the feed mixture may or may not exhibit phase separation in the absence of solid; but the reject hydrocarbon stream (raffinate) should separate from the slurry of solid and solvent. Also, the part of the feed mixture to be extracted into slurry should not dissolve in the slurry in all proportions, particularly if a reflux stream to raise the extract purity is to be employed. The requirement for phase separation over the course of the extraction is of course common in liquid-liquid extraction systems. Introduction of the solid, which may tend to dissolve to a considerable extent in the solvent, may produce slurry-hydrocarbon phase separation by salting-out of the feed components from solution.[43]

It is evident that a nonpolar solid such as perhydrotriphenylene[44, 45] is poorly adapted to this technique, in spite of the wide variety of guest species with which it may form inclusion compounds (the guests range from rare gases to high polymers).

Liquid-liquid phase separations of course depend on nonidealities in solution; whether a given solid complexing substance will cause the necessary phase split may be resolved by experiment in any doubtful case. The term "relatively polar" is admittedly inprecise; it reflects in part the state of scientific understanding of nonideal solutions.

B. Kinetic Factors

A significant property of the slurry extraction technique, in comparison with other systems, has to do with kinetics. The equilibration of all solid present in the moving slurry must be accomplished in a few minutes' time. The reason for this is that the system is basically a multi-stage separation with host and guest being subjected to many equilibrations over the course of the separation. For this to be practical, a long residence time per stage is out of the question, since it would imply a very large volume in each extraction zone, on the already large scale of petroleum or petrochemical operations for which this process was designed. Manning and coworkers found that the rates of formation of urea adduct from solution in alcohol were very high, with the rate-controlling process judged to be diffusion of urea.[46-51] However, the key rate for slurry extraction viability is not necessarily that of adduct precipitation from dissolved components, but may instead be that of transformation of one solid adduct into another, i.e., the exchange rate. This is particularly to be expected when a separation is contemplated of two components, both of which adduct with the host substance, but which form adducts of different stability. However, it has been pointed out that both urea and thiourea tend to incorporate impurities in the adduct by coprecipitation, so the exchange must be fast enough to remove such impurities by equilibration of slurry with purer product. Refluxing is a simple matter if the slurry has been properly designed: choice of the solvent and solid to produce high rates of equilibration is the basic requirement. Experimental definition of the rate depends on

mixing efficiency; this in turn is decreased as the solids content of the slurry increases. Finally, the difference in adduct stabilities of two exchanging guest substances implies that the solids content of the slurry will be concentration-dependent. The author has studied exchange rates in thiourea slurried in 2-methoxyethanol,[10] and has produced evidence for the following preliminary statements:

1. Displacement of guest A from thiourea by guest B will occur at a higher rate than displacement of B from thiourea by A, if A is more soluble in the solution.
2. Relative adduct stability of A and B, in the tests conducted, did not influence the exchange. Since the absolute amount of solid to be exchanged depends on the stability of adduct, the rates of exchange would be expected to reflect such differences. The tests were performed with a large ratio of solid to solution, however, so it seems reasonable that small changes in the ratio could have had little or no effect.
3. Under conditions of good mixing, it is probable that the exchange reactions in thiourea-2-methoxyethanol (ratio of solvent to solid = 2.2/1) take place fast enough to equilibrate the slurry at room temperature in less than ten minutes.

Figures* 1 and 2 show some typical test results. The rate data were taken under conditions unfavorable to maximum rates, to show up the differences referred to. The equilibrium compositions were estimated by mixing the charge proportions of the two guests, added as a single solution to the slurry, and assuming no differences in rate of adduct precipitation. The order of solubility in the solution is methylcyclopentane >cyclohexane >2,2-dimethylbutane,[10] and the adduct stability order is cyclohexane >2,2-dimethylbutane >methylcyclopentane. The only reliable indication of extent of reaction was found to be analysis of the hydrocarbon layer composition;

* Illustrations for this article begin on page 279.

sampling of the other phases or estimation of the quantity of any phase as a function of time was inconvenient. More careful investigation of such systems is indicated. The mechanism of equilibration is thought to be dissolution of guest and host in solvent and rapid precipitation of adduct. The results of Figures 1 and 2 are consistent with the hypothesis of a slow transfer from adduct through solution for guests of low solubility.

C. Equilibrium Considerations

Differences in fit of guest molecules into the incipient cavities in the matrix of host crystal appear to account for variations in stability of solid adduct. The dissociation of urea adduct of substance A is described, per mole of A, by

$$\underset{\text{solid adduct}}{(\text{urea})_m\,A} = \underset{\text{solid}}{m\ \text{urea}} + \underset{\text{liquid}}{A}\ , \qquad (1)$$

where m is the mole ratio of urea to guest in the adduct (not necessarily integral). The equilibrium constant for equation (1) is

$$K_A = (a_u)^m\,(a_A), \qquad (2)$$

where a_u and a_A designate activities of urea and guest, and the activity of complex is unity since the substance is considered to be in its standard state. a_A may be approximated by the mole fraction, X_A, in an ideal solution in nonadducting solvents; then for excess urea ($a_u = 1$),

$$K_A = X_A. \qquad (3)$$

This relation is commonly used to determine adduct stabilities. An alternative method utilizes the equilibrium vapor pressure of guest above adduct. Equilibrium constants have been measured for a number of guests of urea and thiourea.[28, 29, 52]

Examination of equation (3) shows that the equilibrium dissociation constant may be interpreted as the lowest value of the mole fraction of A which can be produced in solution by urea adduct precipitation, regardless of the excess of urea: a "cleanup limit."

Higher adduct stability will be reflected in a smaller value of K. Operationally, this leads to higher recovery of guest from solution.

When two guest species, A and B, are both present, their activities in the solid complex may be represented by their mole fractions on a host-free basis, Y_A and Y_B:

$$K_A = \frac{X_A(a_u)^{m_A}}{Y_A}; \quad K_B = \frac{X_B(a_u)^{m_B}}{Y_B}. \tag{4}$$

Implicit in this discussion is the assumption that A and B go into the same phase of mixed adduct. It is generally observed for urea and thiourea adducts that the adduct crystal structure is independent of guest,[9, 18] so that the solid may be considered a single phase solid solution of varying composition.[28] The separation factor, defined by

$$\alpha = \frac{Y_A X_B}{Y_B X_A}, \tag{5}$$

is just the quotient K_B/K_A if $m_A = m_B$, or if excess host is used. Again, for excess host, if A and B are the only guests, then

$$Y_A + Y_B = 1, \text{ or } \frac{X_A}{K_a} + \frac{X_B}{K_B} = 1. \tag{6}$$

Equation (6) describes the phenomenon of co-complexing, where the adduct structure is stabilized by more than one species. Substances which do not normally complex (K > 1) may be adducted if sufficient guest is present, or guest A may be depleted in the solution below its normal equilibrium limit by co-complexing with guest B.[28, 38]

Liquid-liquid equilibrium is also attained between the solution part of the slurry and the raffinate. The same factors which lead to liquid-liquid immiscibility in simpler systems obtain. Dissolved solid, however, strongly influences the distributions, because of strong salting-out effects. As the extraction proceeds in the direction of slurry loaded with pure extract, it often hap-

pens that the maximum concentration of solid adduct is approached. This corresponds to maximum removal of dissolved solid from solution, and a simultaneous minimizing of the salting-out effects. The liquid-liquid distributions must therefore reflect a continually changing environment.

All these factors have been put into a semiquantitative form by the author.[10] For the distribution of A and B between raffinate and slurry,

$$\alpha = \frac{\frac{(a_u)^{m_A} C}{K_A} + K_{DA} S}{\frac{(a_u)^{m_B} C}{K_B} + K_{DB} S}, \qquad (7)$$

where C represents the number of moles of guest in solid, S is the total moles of solution, and K_{DA} and K_{DB} are the molar distribution ratios, i.e.,

$$K_{DA} = \frac{\text{moles of A in solution/S}}{X_A}, \qquad (8)$$

K_{DA} and K_{DB}, because of the salting-out effects described, will not be constant. The selectivity according to equation (7) will vary as the ratio of solid to solution changes. Operationally, one uses (7) mainly as a correlation device, since solubilities, distribution ratios, and host activities are not generally calculable. The capacity of the slurry is $C + S\,[K_{DA}X_A + K_{DB}X_B]$. In separations which may best utilize slurry extraction, none of the capacity terms are negligible. For example, if $K_{DB}X_B$ could be made consistently much smaller than $K_{DA}X_A$, the separation could be readily done by conventional liquid-liquid extraction, with α simply the ratio of the K_D values. The solution capacity is regulated partly by the demand made for rapid equilibration of the system at each stage of the separation, so the second term in the slurry capacity cannot be negligible in comparison with the solid extract C. The maintenance of pumpable slurry is related

to the ratio C/S, which in any realistic system has maximum limits; this also controls the relative size of contributions to the capacity.[10]

IV. An Illustrative Separation

Methylcyclohexane forms a thiourea complex, of low stability.[29] n-Octane does not complex with thiourea under normal conditions, but since n-heptane, n-decane, and octene-1 are reported to be co-complexed, it is expected to appear in complexes with methylcyclohexane.[38] Similarly, m-xylene is reported to co-adduct.[38] A feed stream containing only these three substances may be treated with thiourea-2-methoxyethanol slurry to extract the two cyclic hydrocarbons and produce raffinate of n-octane. Urea slurry, to produce raffinate of methylcyclohexane, could operate on the same feed mixture.

The flow plan is shown in Figure 3. Suppose the feed mixture to be treated, the extract product, and the raffinate product are as shown in Table I. The problem is to devise a scheme which will do the separation with a reasonable minimum of slurry, stages of extraction, and product reflux.

TABLE I

Composition of Process Flow Streams

Stream:	Feed	Extract Product	Raffinate Product
m-Xylene	20 wt.%	35%	1%
Methylcyclohexane	40	60	14
n-Octane	40	5	85

A. Phase Equilibria

The system contains five components: thiourea, 2-methoxyethanol, and the three components of the feed mixture.

The experimental results were obtained at 25°C and atmospheric pressure. The maximum number of phases is four, by the phase rule.[53] No attempt at a pictorial representation of the total system will be made here, nor will the final process design be produced; such detail is better left to electronic computation. Instead, laboratory results will be presented in the form of ternary system diagrams, drawn on a weight basis.

In Figure 4, the solvent-paraffin-aromatic system is shown. As an extractant to separate these two hydrocarbons, 2-methoxyethanol is obviously inadequate: solutions of m-xylene in octane more concentrated than 34 wt.% are miscible with solvent in all proportions. (In these figures, solid points refer to charge compositions and open circles to analysis results.)

Similarly, Figure 5 indicates that xylene (p-xylene in this case)-solvent-methylcyclohexane mixtures are all but completely miscible. The remaining liquid-liquid system of interest is shown in Figure 6.

Solutions of urea and polar solvents have been proposed as extractants.[54] The effects of dissolved species would be expected to be an increase in selectivity for aromatics over paraffins, for example, coupled with a sharp decrease in capacity for hydrocarbons dissolved in solution. Qualitatively, such effects are understood by "salting-out" of the dissolved hydrocarbons. The urea (or other polar solute) evidently interacts much more strongly with solvent than do hydrocarbons, which are forced out of solution in the competition.[55-56] In Figure 7 the salting-out effect of dissolved thiourea on the m-xylene-n-octane-2-methoxyethanol system is seen to produce a two-phase region much larger than that of Figure 4. To make the system comparable with others in this series, the ratio of 2-methoxyethanol to thiourea was held constant in the charge at 2.2. The undissolved solid phase is included in the heavy phase composition. The amount of solid is shown separately. Such a "pseudo-ternary"

representation is useful in interpretation of slurry systems, when the solid may contain one or more of the hydrocarbons. The solid in this system is expected to be pure thiourea. Changes in selectivity are quite large, as shown in Figure 8. Here the selectivity is in terms of the separation factor [equation (7)].

A system to compare with Figure 5, for the possible separation of m-xylene from methylcyclohexane (Figure 9), must utilize some salting-out agent other than thiourea, to avoid the complication of thiourea-methylcyclohexane adduct. The effect is well illustrated with urea slurry. For our purposes, it is of interest that a mixture of m-xylene and methylcyclohexane in the proportions of the proposed extract product (37% m-xylene) will probably not cause loss of phase due to miscibility, from salting-out considerations alone. This prediction is borne out by examination of the actual slurry system, to be discussed later on.

The use of slurries as extractants maximizes the salting-out effect, since solids are vital to the separation, and the liquid phases are constantly saturated with respect to solid complexer or solid adduct. The effect is limited, in purely liquid-liquid extractions, by the lower concentrations of salting-out agent necessary to avoid precipitation of the solid phase.

In Figures 10, 11, and 12, the three hydrocarbon-solvent-thiourea ternaries are presented as background for the slurry equilibrium studies. Figure 10 shows complete miscibility of the two liquids and some solubility of thiourea in the liquid phase, but no other features. There are five experimental points in Figure 11, as a result of the low miscibility of 2-methoxyethanol and n-octane. When the hydrocarbon is methylcyclohexane (Figure 12), the diagram becomes much more complicated because of solid adduct formation. Figures 10-12 are schematic only in that the additional data necessary to define line curvatures along ED in Figure 10, FB and GE in Figures 11 and 12, and the precise location of points

E and K were not determined. Some idea of how much the system is complicated by nonidealities can be inferred from Figure 13, which incorporates an "ideal solvent" in place of 2-methoxyethanol. The molecular weight of this hypothetical liquid is the same as that of methylcyclohexane, so that the minimum concentration of methylcyclohexane in equilibrium with thiourea adduct is 43 mole %. The solution L, of negligible thiourea content, is an ideal solution, so that by equations (2) and (3), $K_{MCH} = 0.43$. In practice, if a truly non-adducting solvent is utilized, and if its solutions with methylcyclohexane are close to ideal, some activating polar solvent is used in trace quantities to bring the system to equilibrium. The solvent is "ideal" for purposes of definition of K_{MCH}; it is emphasized that for slurry extraction, the failure to provide liquid-liquid phase separation would almost certainly remove it from consideration even if rate considerations did not.

In an extraction process, slurry must flow through the extractor and other process equipment whether it is loaded or not. The minimum 2-methoxyethanol/thiourea weight ratio tolerable for slurry loaded with cyclohexane has been found to be 2.2.[10] If this ratio is set for the current system, Figure 12 shows that "empty" slurry, at 68.8% 2-methoxyethanol on the AB boundary, will contain 2.3 weight percent solid thiourea. If the slurry is loaded with methylcyclohexane, it will attain the composition of point M, containing 27 weight percent solid adduct. The possibility of generating thicker slurry than this must be avoided in the process scheme. Extensive washing of slurry with pure methylcyclohexane would eventually remove solvent catastrophically. In operation, this means that reflux washes to the extractor should contain solvent, to some extent.

Figures 14 and 15 are pseudo-ternary representations of slurry equilibrated with two pairs of hydrocarbons. Points M and H are the same as in Figure 12. The "binary" slurry-octane

points are obtained similarly from Figure 11. Since methylcyclohexane is the only hydrocarbon of the three to form a stable thiourea complex, the trend in both Figures 14 and 15 should be to maximum adducted hydrocarbon as the A-C boundary of the ternary is approached. This is observed, but with a major difference: in Figure 14, the amount of thiourea in the solid increases strongly with increasing methylcyclohexane, while in Figure 15, most of the thiourea charge is found in the solid phase in any case. The explanation for this is doubtless tied to the relative solubilities of thiourea and hydrocarbon in the solution. The solubility of n-octane in 2-methoxyethanol is so low that its presence does not significantly affect thiourea solubility; the solvent is about as effective to dissolve thiourea as if no hydrocarbon were present unless the proportion of methylcyclohexane is increased. On the other hand, m-xylene and solvent are miscible in all proportions (Figure 10). In this case, dissolved xylene keeps thiourea out of solution. These results are shown graphically in Figure 16. Experimentally, very little solid remains at high octane content, as reflected in the low slurry capacities for hydrocarbon shown in Figure 14. Because the proposed process raffinate is mainly octane, this effect can complicate the design somewhat. Modifications of the process can be introduced to raise the slurry capacity, as will be described. Selectivity of the solution for methylcyclohexane over n-octane also changes with hydrocarbon composition (Figure 17); this is not unexpected in view of the same effect evident in the non-adducting systems of Figures 7 and 9. The results of Figures 14, 16, and 17 were used to predict tie-line (7) in Figure 14, which was difficult to define experimentally because of low hydrocarbon and solids content in the slurry.

An invariant zone of four phases appears in Figure 15, because of the major fraction of undissolved thiourea in the region of limiting adduct stability (DEF). In this region, the

two liquid phases coexist with solid thiourea and solid adduct. As the charge composition changes, the relative amounts of the four phases may change, but the compositions of all phases remain constant. Point D then represents the composition of the slurry leanest in methylcyclohexane which can coexist with raffinate of composition F without generation of uncomplexed solid thiourea. Slurries leaner in methylcyclohexane than described by point E contain no adduct, only solid thiourea.

Material balance indicates some co-complexing for the systems described by Figures 14 and 15. Detailed analysis of the solid phases, together with corrections for nonideality, would permit estimation of the equilibrium dissociation constants for the unstable n-octane and m-xylene adducts with thiourea, but for purposes of the present discussion, the experimental definition of Figures 14 and 15 is considered adequate.

A region similar to DEF in Figure 15 must exist in Figure 14, but its size is much smaller because of the increased solubility of thiourea in the solutions. An added complication is the greater tendency of n-octane to co-complex.

B. System Design

The equilibrium data indicate that the desired separation may be accomplished by slurry extraction. In this section, some of the facets of system design will be examined.

Simple graphical techniques are available for estimation of stages, reflux, and extractant requirements in true ternary systems.[57] By the use of these methods, one may get a basis for comparison of possible alternatives. The best calculations, as was mentioned, utilize electronic computations, and are not limited to simple systems. However, this discussion is meant to be descriptive, not exhaustive, in its treatment of the methylcyclohexane-m-xylene-n-octane system, so simple techniques will suffice.

For the recovery section of the extraction unit, the key separation is that of methylcyclohexane from n-octane, because (1) the high selectivity of slurry for m-xylene from octane and the relatively low concentration of m-xylene in the feed indicate that it will not be present to any great extent in the raffinate end of the separation, and (2) conditions indicate a minimum of methylcyclohexane adduct formation as the hydrocarbon phase approaches the raffinate concentration (Figures 14 and 16).

Choice of a key separation in the rectification section of the extractor (between the feed plate and the point of removal of loaded slurry) is less obvious. The high concentration of aromatics in the extract will tend to magnify the equilibrium solubility of n-octane in solution, although examination of Figure 7 indicates that the effect would be small even if no methylcyclohexane were present. Because the solution selectivity for m-xylene over n-octane is greater than that for methylcyclohexane over n-octane (Figures 8 and 17), the net solution selectivity for extract will be higher than if aromatics were not present. Since only 60% of the extract can form adduct, the solid contribution to slurry selectivity will be proportionately reduced. The sum of these considerations might not change the separation greatly from the slurry methylcyclohexane-n-octane system of Figure 14. This system is, therefore, a reasonable facsimile of the illustrative process.

It is emphasized that our choice of feed components and proportions leads to the use of the methylcyclohexane-octane separation as a key in both sections of the extraction. Thiourea with guest species other than methylcyclohexane forms much more stable adducts.[29] In a feed mixture of cyclohexane-m-xylene-n-octane, for example, the adduct would be about twenty times as stable as methylcyclohexane adduct, and the key separation might then be that of m-xylene from n-octane.

Characteristics of two separations are shown in Table II. Both treat a feed mixture of 50% methylcyclohexane in n-octane to produce extract of 92.33% methylcyclohexane and raffinate of 14.14% methylcyclohexane. The slurry calculations are taken from Figure 14; the solvent case is based on Figure 6. A better solvent case could be made with the use of a salting-out agent, but thiourea and urea form adducts with methylcyclohexane and n-octane, respectively, so their use is precluded here. Extension to other salting-out agents or better solvents[58,59] for the separation of naphthenes from paraffins is outside the scope of this discussion. 2-Methoxyethanol does show a good selectivity

TABLE II

Separation of Methylcylohexane from n-Octane

Case	1.	2.
Extractant	Thiourea Slurry	2-Methoxyethanol
Equilibrium Stages:		
Recovery	4	7
Rectification	6	6
Extractant/Feed	11.5	17.1
Reflux/Product	1.9	16.5

for this particular separation, however, so its use in case 2 is acceptable for comparison with the slurry system. The greater selectivity of thiourea slurry in this separation leads to more complete rejection of n-octane from extract going from the feed plate into the rectification section, with concomitant savings in extractant and reflux.

Various refinements to the extraction may be made. Selectivity is critical in the recovery zone, where the amount of

solid is minimal. If the thiourea to solvent ratio in slurry were increased in this part of the process, the adduct contribution (as long as adduct is stable) could be increased. Provision can be made for adding solvent at a subsequent point in the extraction, when the concentration of methylcyclohexane has increased, so as to avoid the generation of excessive solids.[51] Change of temperature can be utilized to generate reflux or manipulate the phase equilibria.[26] Addition of complexing guest substances to the system allows a lower concentration of methylcyclohexane in the raffinate (better recovery).[60,61]

V. Outlook

Assuming that the problems of kinetics and equilibrium can be solved along the lines discussed, so that a slurry extraction process could be attractive, one must then deal with a number of operational questions, such as:

1. Will the slurry flow as an entity through the process? The concern here is whether solid will settle out of suspension in the solution and tend to accumulate as it moves at a different rate from the solution. It is true that thiourea-2-methoxyethanol slurry has been run continuously in a demonstration unit in the author's laboratory, but long-term and rigorous testing of the flow characteristics of any slurry mixture should be insisted upon.[62]
2. What are the proper storage conditions for the slurry? Daily temperature changes can result in the growth of large crystals of solid thiourea and dissolution of small particles.[10] A key parameter in slurry flow is particle size, so reasonable precautions must be taken against its uncontrolled variation. Possibilities include storage at a temperature high enough to dissolve the thiourea or careful control of storage temperature.

3. How are slurry components removed from the finished products? In Figure 3, the octane raffinate presumably emerges from the extractor saturated with slurry solvent and thiourea. Means to recover the slurry components from raffinate must be provided, because of product quality and slurry materials cost considerations. Similar finishing of the extract is necessary. A number of process options exist for regeneration (i.e., separation of extract from loaded slurry so that the slurry may be recycled to the extractor) of the slurry.[10]

The problems on the way to large-scale operation of a slurry extraction process seem amenable to modern engineering technology. Certainly the technique offers much by way of unusual and efficient separations, for which there is always a demand.

VI. Bibliography

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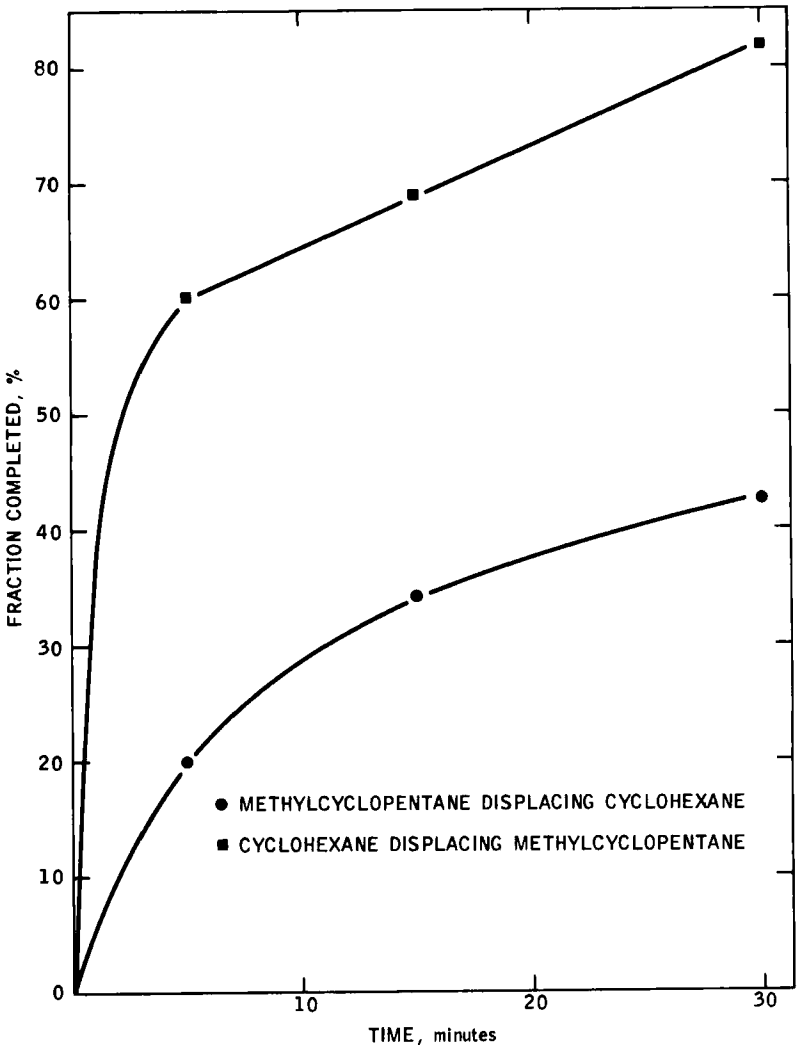

FIGURE 1
Exchange in Thiourea Slurry
25°C

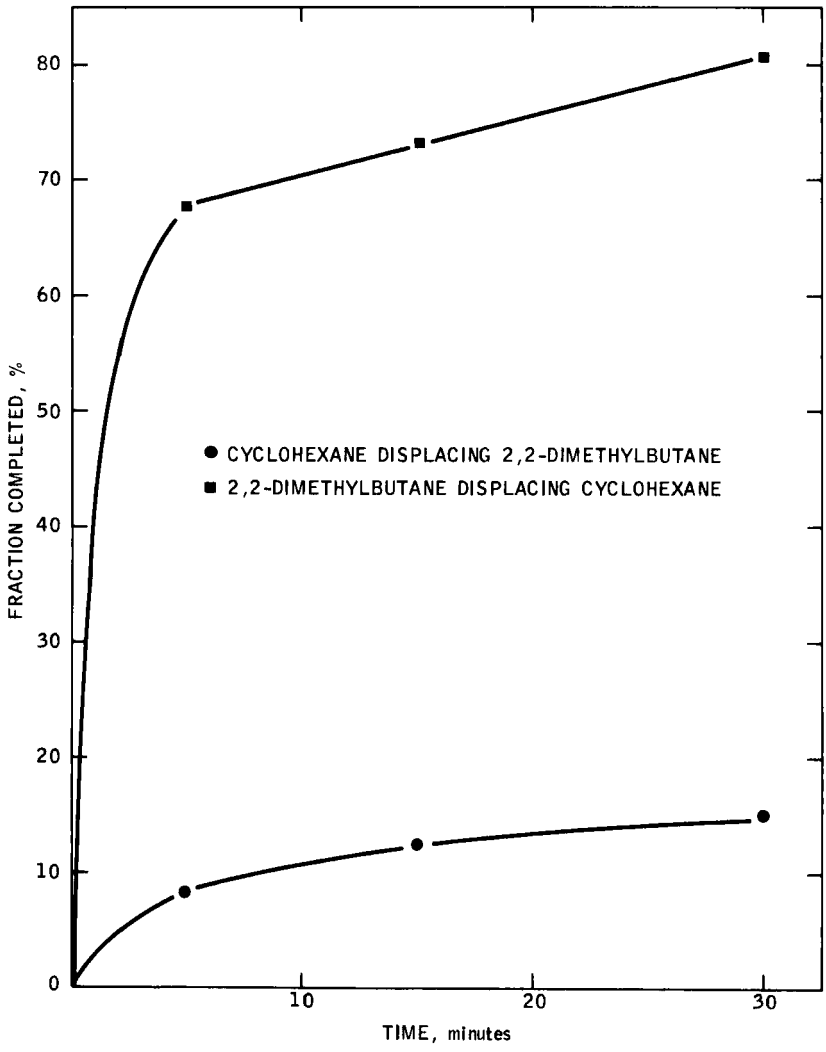

FIGURE 2
Exchange in Thiourea Slurry
25°C

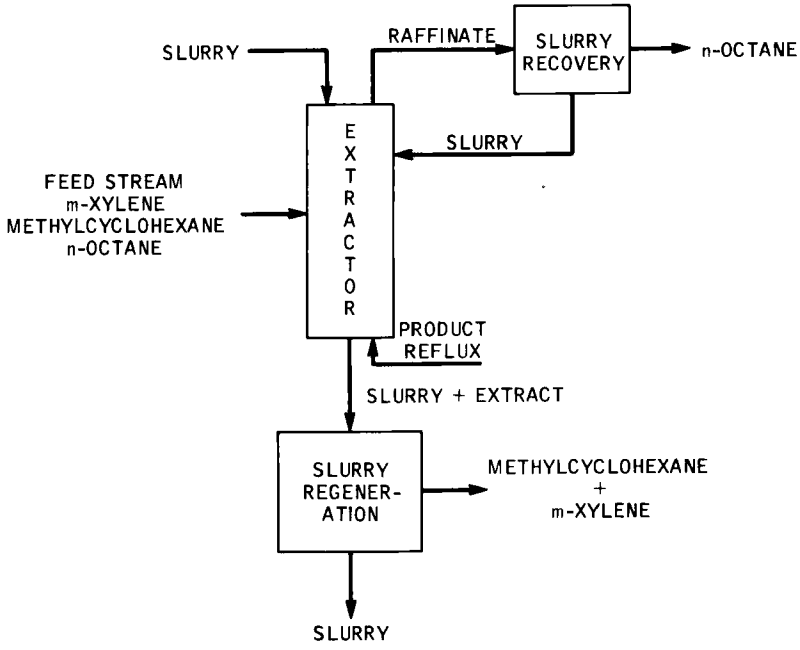

FIGURE 3
Slurry Extraction Flow Plan

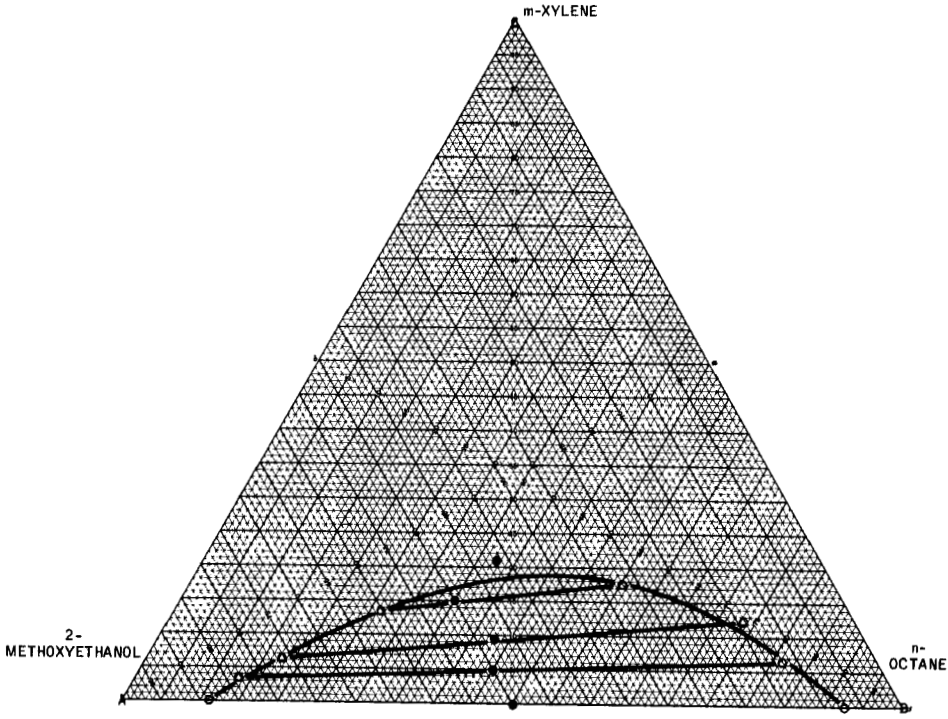

FIGURE 4
2-Methoxyethanol-m-Xylene-n-Octane System
25°C

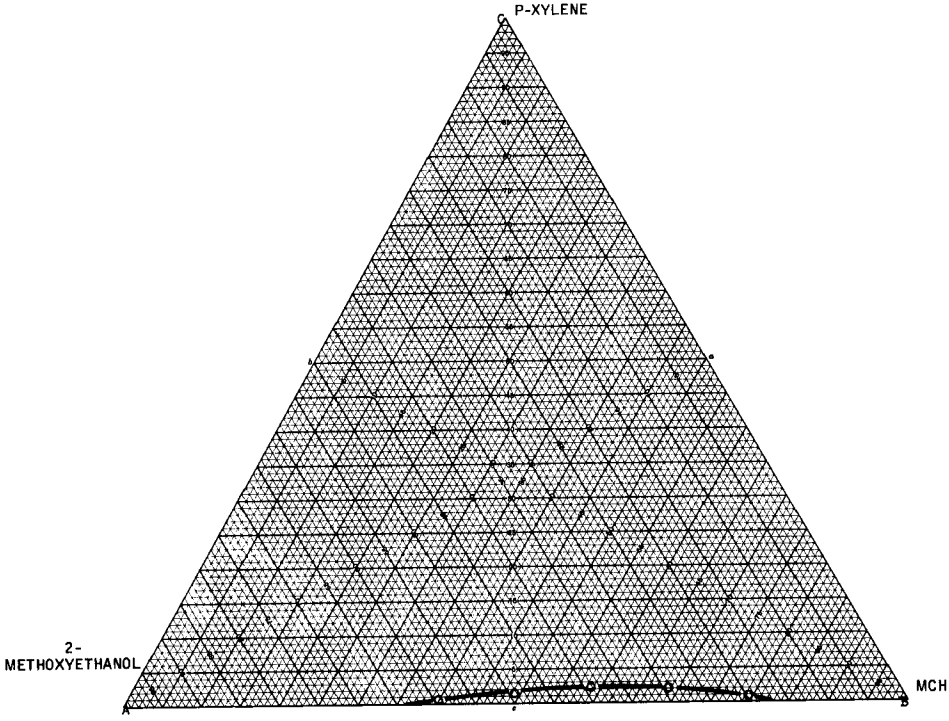

FIGURE 5
2-Methoxyethanol-p-Xylene-Methylcyclohexane
25°C

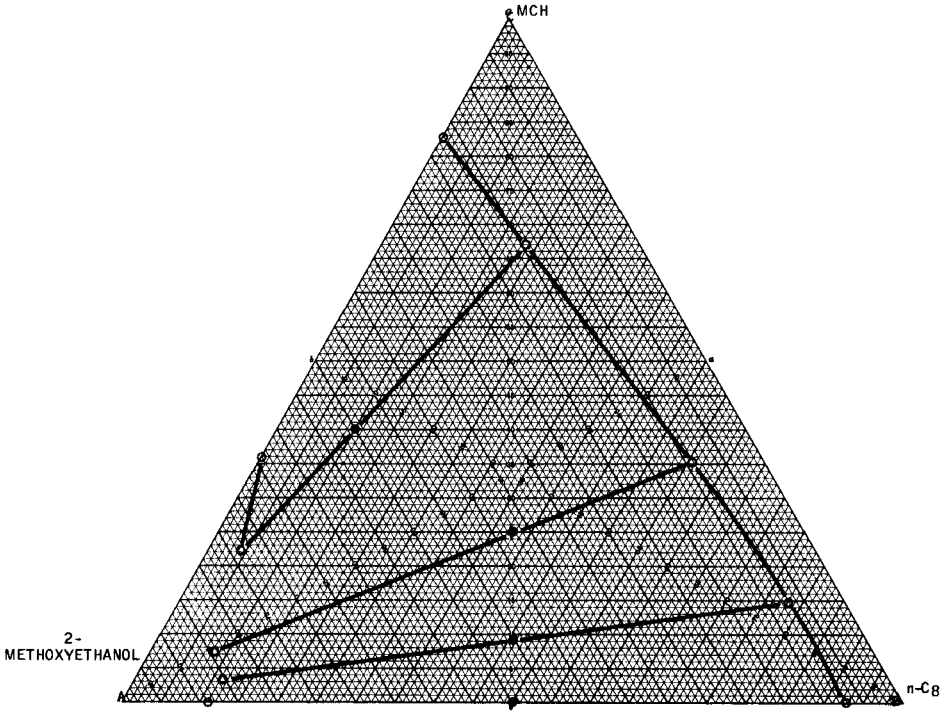

FIGURE 6
2-Methoxyethanol-Methylcyclohexane-n-Octane System
25°C

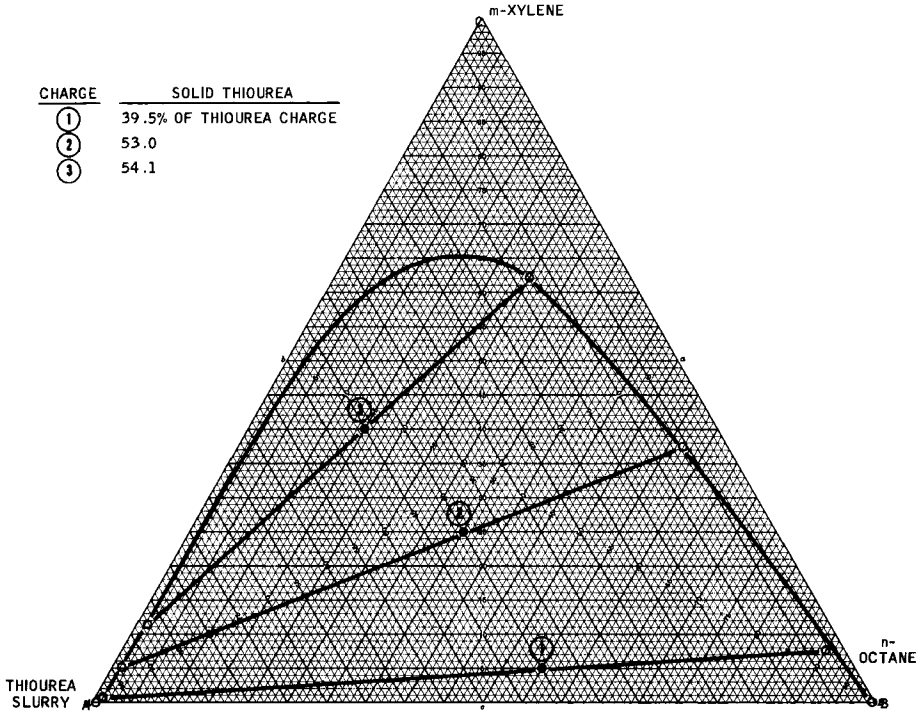

FIGURE 7
Thiourea-2-Methoxyethanol +
m-Xylene + n-Octane
25°C

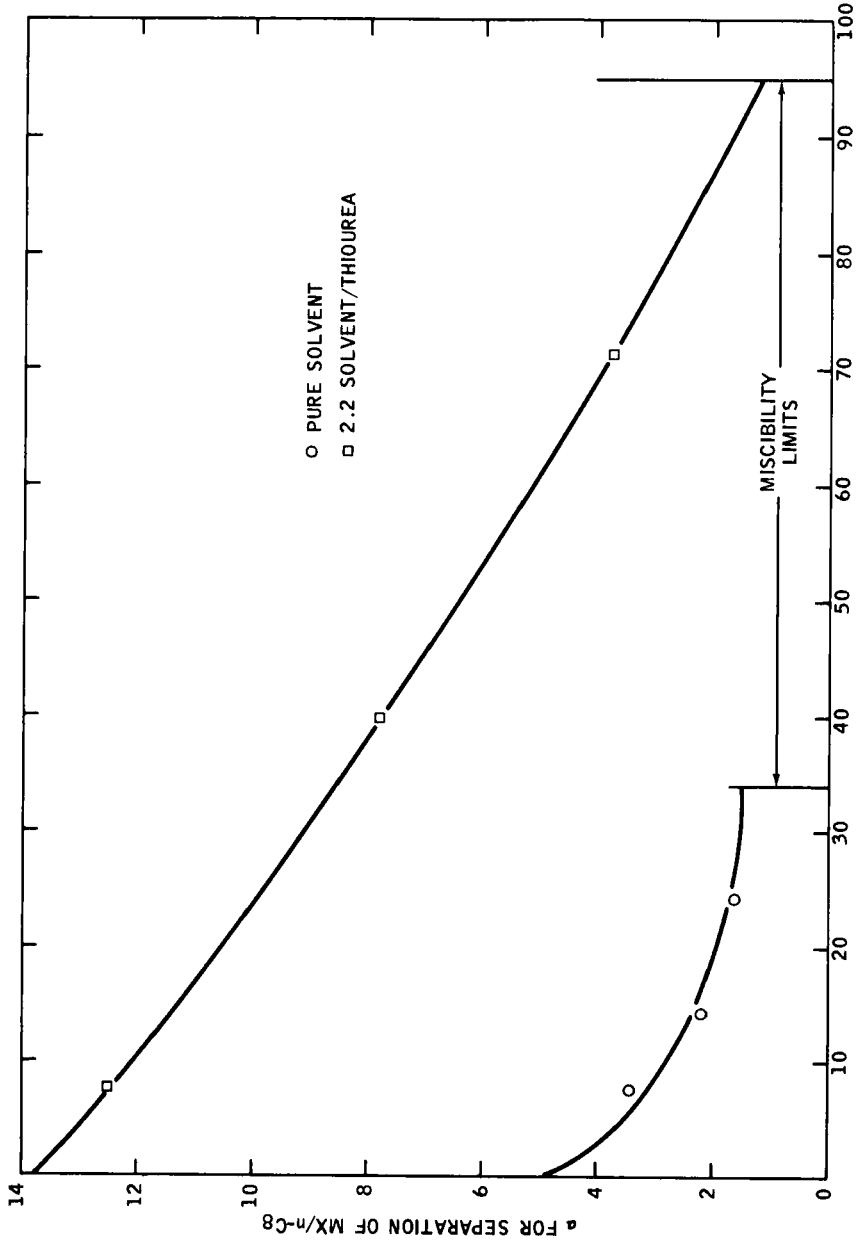

FIGURE 8: Effect of Dissolved Thiourea on Aromatic/Parrafin Selectivity

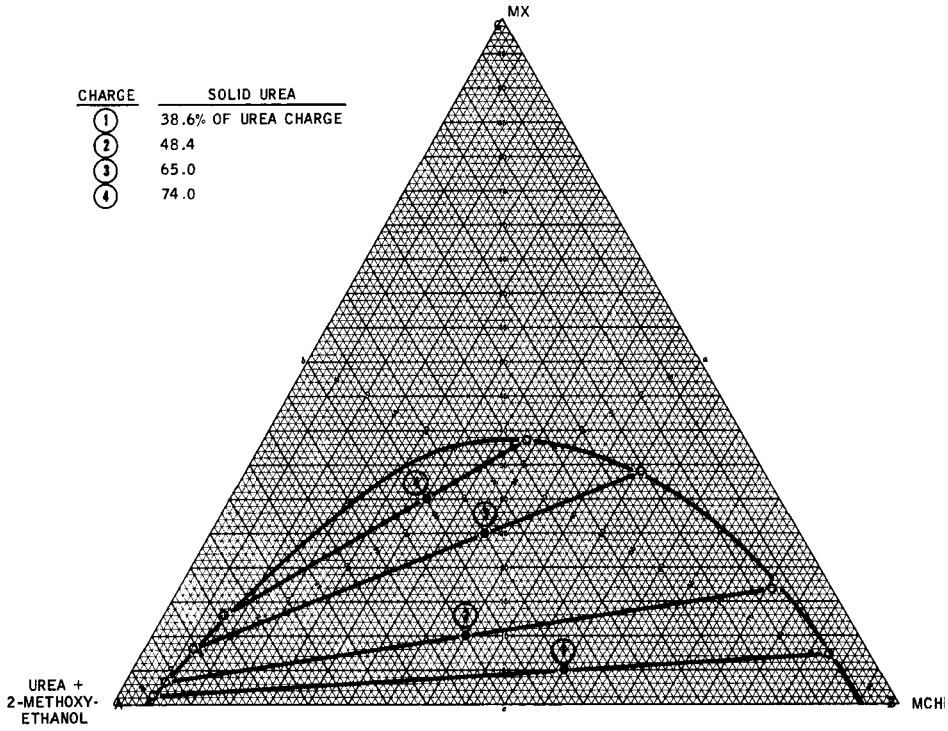

FIGURE 9
Urea Slurry + m-Xylene
+ Methylcyclohexane
25°C

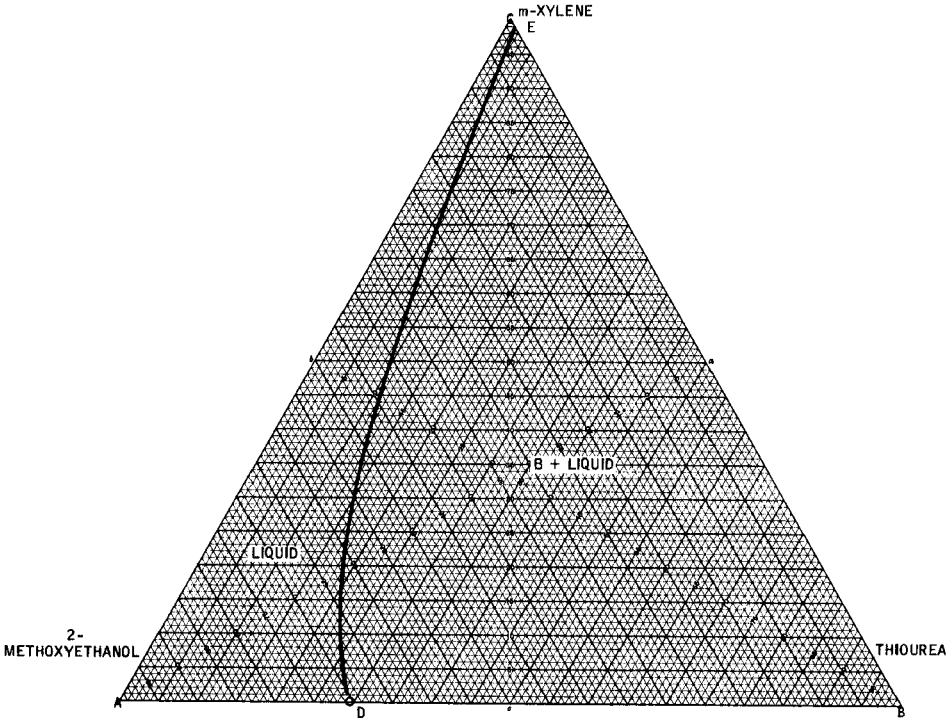

FIGURE 10
m-Xylene-Thiourea-
2-Methoxyethanol (Schematic)
25°C

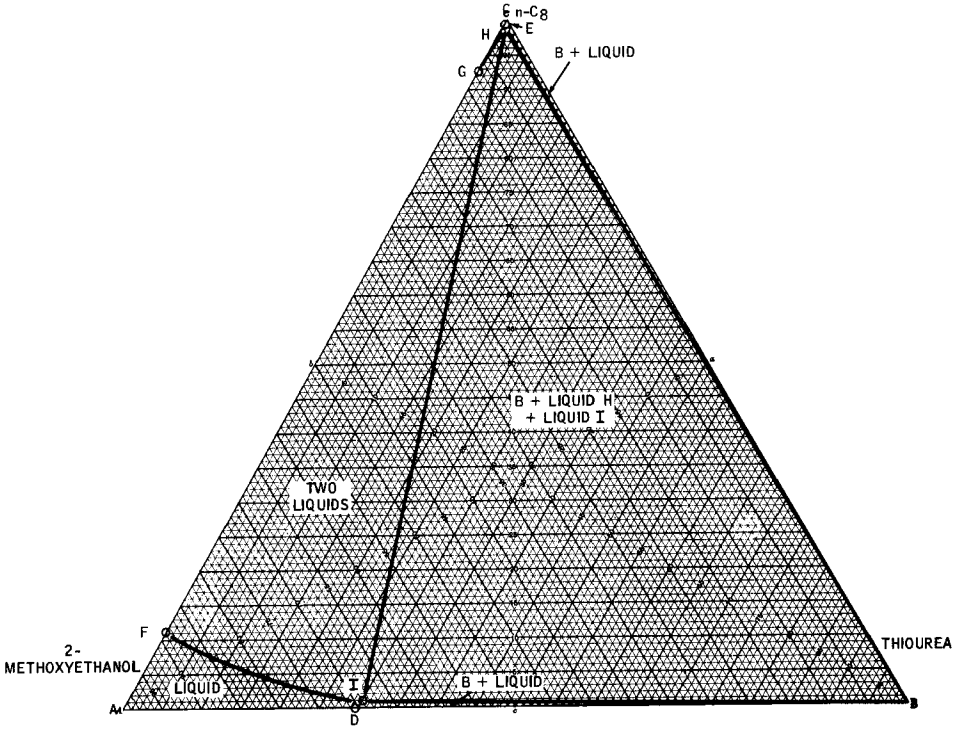

FIGURE 11
n-Octane-Thiourea-
2-Methoxyethanol (Schematic)
25°C

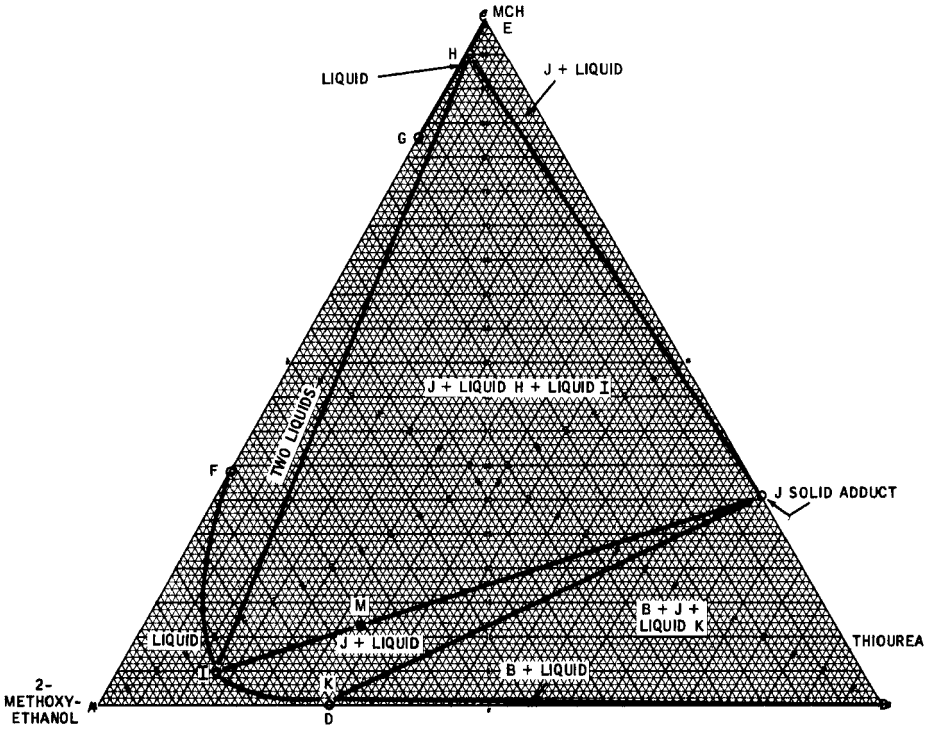

FIGURE 12
Methylcyclohexane-Thiourea-
2-Methoxyethanol (Schematic)
25°C

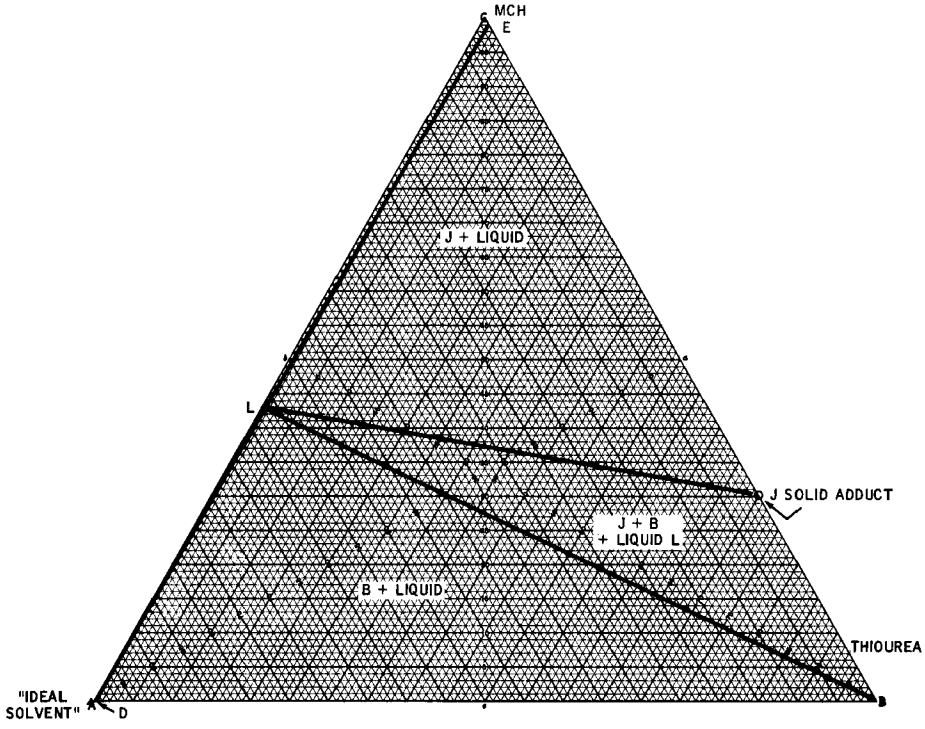

FIGURE 13
Concent of the "Ideal Solvent"

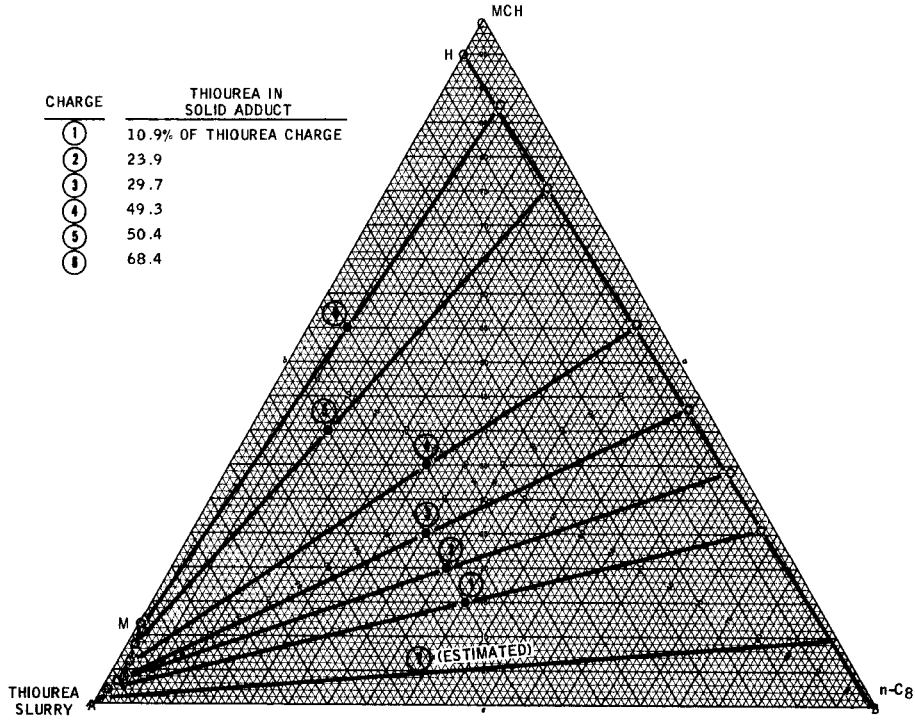

FIGURE 14
Methylcyclohexane-n-Octane-Slurry
25°C

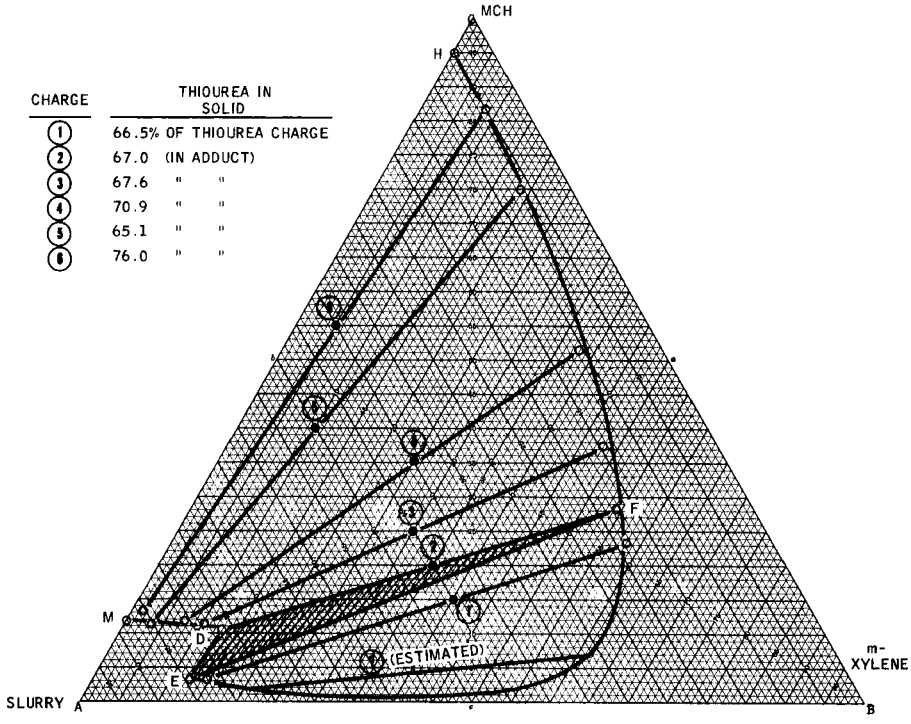

FIGURE 15
Methylcyclohexane-m-Xylene-Slurry
25°C

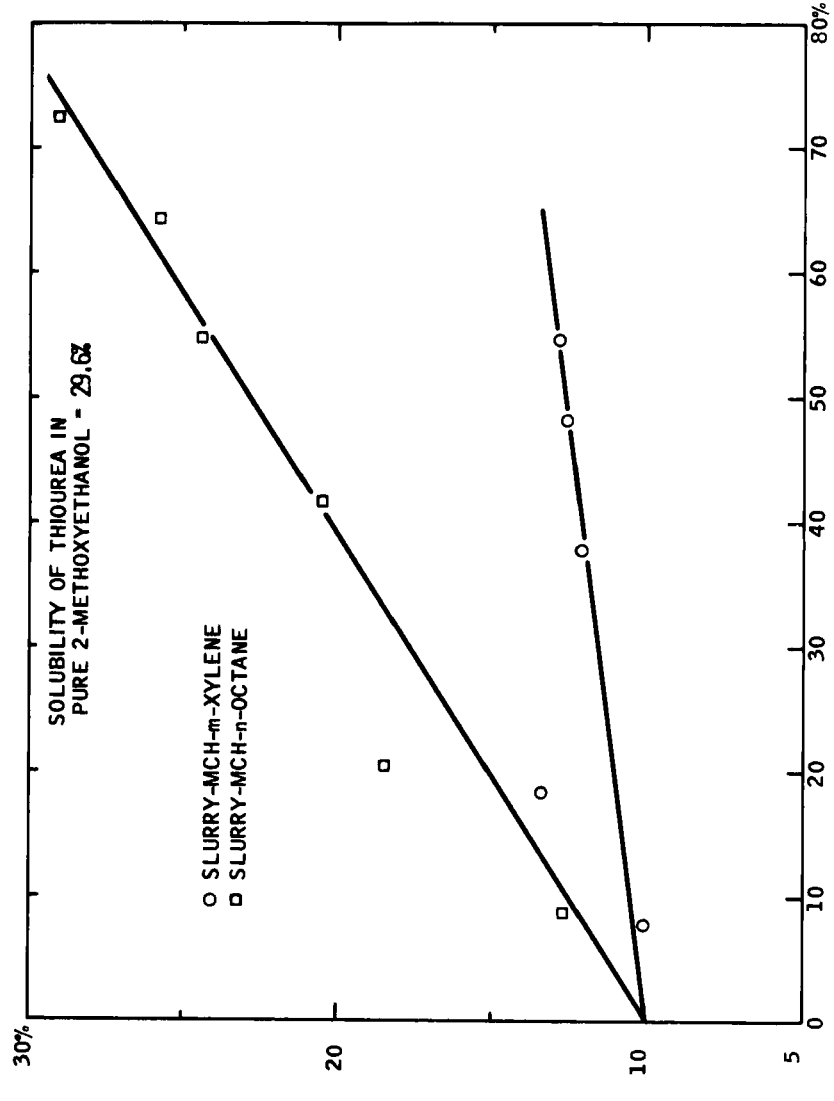

FIGURE 16: Thiourea Solubility Depends on Hydrocarbon Composition

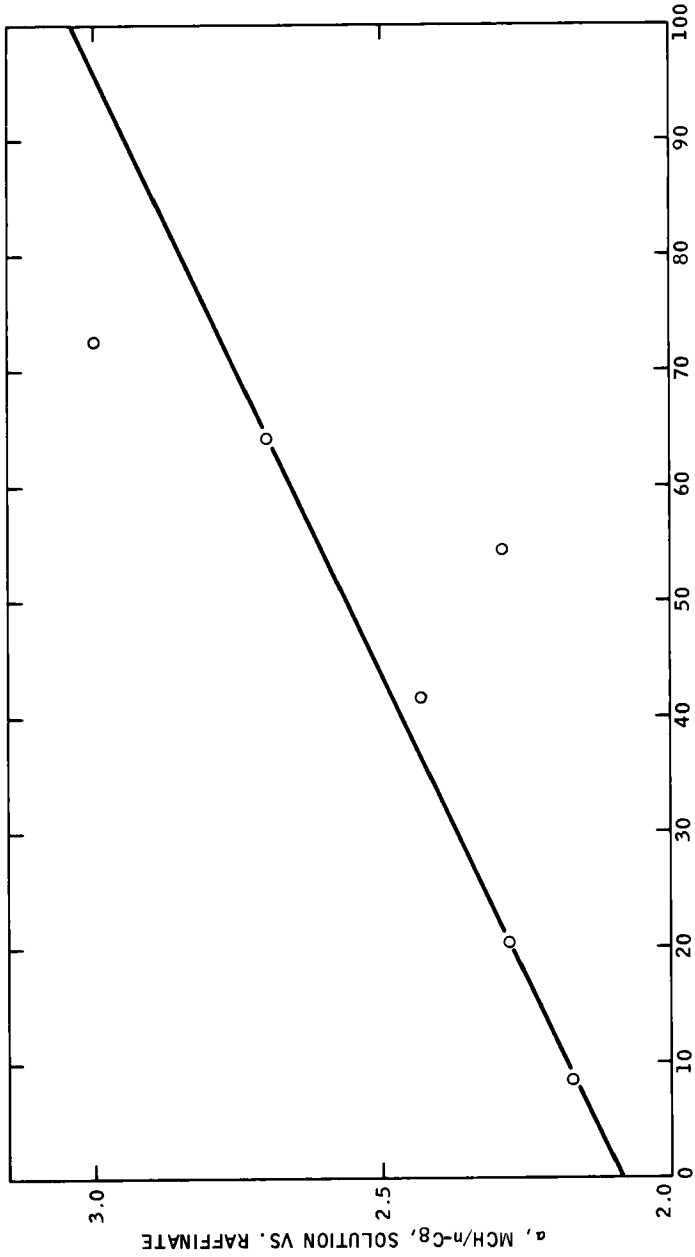

FIGURE 17
Solution Selectivity for
Methylcyclohexane/n-Octane
25°C