ABSTRACT

Title of Thesis:

 LIQUID-VAPOR EQUILIBRIA AND HENRY'S LAW CONSTANTS FOR VOLATILE
ORGANICS IN SURFACTANTS

Qianping Peng, M.S. Environmental Science, 1991

Thesis directed by: Dr. Joseph W. Bozzelli

 We present liquid vapor equilibria data and Henry's law con-
stants for Methyl-ethyl Ketone, Toluene, Butyl Acetate, Acetone
and i-Propanol in surfactants: Octylphenyl Decaethoxylate, Sorbi-
tan Monooleate and Sodium Sulfonate at temperatures of 20 to
70 C.

The objective of this study is to determine the effect of
applying surfactant absorption technique (neat surfactants) to
volatile organic compounds (VOC's) for the removal of these
species as organic vapors from air emission streams.

 Liquid/vapor equilibrium data are presented as curves in sever-
al different ways:

i. Each individual VOC at four temperatures between 22 C to 70 C in the respective surfactants Octylpenyl Decaethoxylate, Sorbitan Monooleate and Sodium Sulfonate. Liquid phase concentration ranges vary for 0.05 to 0.45 mole fraction.

ii. Vapor/liquid concentrations for all the 5 organics in the respective surfactants. At the individual temperatures : 22 C 40 C, 60 C and 70 C. Liquid phase concentration ranges vary for 0.05 to 0.45 mole fraction.

iii. Vapor/liquid equilibria data for each organic at the four respective temperatures in all surfactants (the different absorption capacity of each surfactant).

Vapor concentration data was determined through use of gas chromatography. Analyses of vapor samples over the liquid at the equilibrium was achieved.

All the surfactants provided significant absorbent capacity for the VOC's efficient except for Acetone.

This study determined that the application of pure surfactant scrubbing to absorb the organic vapor is very promising.

LIQUID-VAPOR EQUILIBRIA

AND Henry's LAW CONSTANTS FOR VOLATILE ORGANICS

IN SURFACTANTS

BY

QIANPING PENG

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the New Jersey Institute of technology

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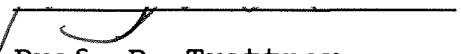
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I. INTRODUCTION

A. Air pollution and its control techniques

Potentially undesirable chemicals are increasingly under scrutiny by the environmental community and regulatory agencies. and at least one group of chemicals -- organic solvents -- has been subject to close scrutiny by air pollution control officials for longer time than most(1).

The reason is twofold: First, many solvents contain or give rise to hydrocarbons in the atmosphere believed to be precursors to the formation of photochemical smog; second, many are strong smelling and have been behind much of the public's increasingly vocal dissatisfaction with industrial odors; here complaints to regulations have become increasing significantly in recent years. It takes more than industrial solvents to produce smog, of course. Current thinking about the smog formation process is that reactive hydrocarbons from several sources combine with oxides of nitrogen stemming to produce "oxidants" under certain conditions of meteorology, energy from sunlight(1). The oxidants consist of a number of different gases and aerosols.

Estimates by the Environmental Protection Agency (EPA) indicate that about 40% of the hydrocarbon emissions arise from industrial operations and organic solvent evaporation(1). Collec-

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tively, they release about 850,000 tons of volatile organic compound annually to the atmosphere with the largest individual sources each being responsible for over 1,000 tons per year.

Effluent air containing organics is a common problem in the chemical, petroleum, synfuels, varnish, cosmetic, dry cleaning, metal degreasing and other industries which are involved in the coating, printing, painting and similar process. These organics are often toxic and must be removed from air before its release to meet emission control requirements.

Obviously, public opinion and broad regulations like those in New Jersey and other states are forces to be reckoned with by users of organic solvents, and they are looking about for -- and finding -- effective ways to control emissions.

The control of hydrocarbon vapors from technological sources rests upon several basic principles(2). These include:

(1) Optimization of combustion processes.

(2) Recovery by mass transfer principles, eg: condensation or adsorption.

(3) Restriction of evaporative loss.

(4) Substitution of process materials with other having different chemical or physical properties.

Control principles used for stationary sources of emissions and evaporations of organic substances include:

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(1) Evaporation prevention

(2) Incineration

(3) Adsorption

(4) Condensation

(5) Substitution of less volatile and less photochemically reactive
   materials in solvents

(6) Flaring

(7) Absorption

(1) Evaporation Emission Controls:

The direct control of the evaporation involves, as a general
principle minimizing liquid-air contact. The major opportunities
for this control measure are in the storage and transfer of
materials. These systems are normally used only with hydrocarbons
of rather high vapor pressure.

(2) Control by Incineration

One method to control emissions is incinerating the gases so
that the hydrocarbons are totally oxidized to carbon dioxide and
water. This combustion process which generates energy, elimi-
nates product recovery. It is used only if the products of com-
bustion are innocuous. It is not recommended to attempt control
organic vapors containing halogens, sulfur, or nitrogen solely by
combustion. Possible adverse environmental effects must be con-
sidered in choosing incineration as a means of controlling vola

tile organic vapor emissions. Many commercial processes are available, some employing catalysts. Direct flame incineration can be used where the solvent is present in sufficient concentration to sustain combustion. More commonly, thermal incineration is employed, and an auxiliary fuel supplies the heat necessary to raise gas temperature above the autoignition temperature of the organic constituents. Use of a catalyst lowers the temperature needed to ensure combustion, but catalyst life may be limited.

(3) Control by Adsorption

Adsorption is the process by which components of a gas are retained on the surface or in the pores of granular solids(3). The solid adsorbent particles are highly porous and have a very large surface to volume ratio. Gas molecules penetrate the pores of the material and contact the large surface area available for adsorption. Organic vapors retained on the adsorbent can be subsequently desorbed, far recovery or regeneration . Both the vapors and the adsorbent are recovered and may be reused. Adsorption occurs primarily through two mechanisms:

a. physical adsorption in which Van Der Waals' forces attract and hold gas molecules to the adsorbent surface.

b. chemical adsorption, in which gas molecules are chemically bonded to the adsorbent.

Both chemisorption and physical adsorption are exothermic processes; the heat released from adsorption is on the order of 5 - 10 kcal/g-mole(4). If the gas or vapors to be adsorbed consist

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of several compounds, the adsorption of the various components is not uniform.

Activated carbon has a very high affinity for organics(5), and therefore its use in air pollution is widespread. However its use is limited to adsorption of in low concentrations steams because of the necessity for frequent regeneration. The high initial costs, are the primary reason which made installations are held down. Concentrations of organics greater than 25 percent of the lower explosive limit are undesirable because the heat released by adsorption may raise the temperature of the carbon bed high enough to cause combustion.

(4) Control by Condensation:

Condensation is the process by which vapors are converted from gases to liquid by cooling. This technique is most suitable for high concentrations of organics since substantial quantities of a vapor may exist with its liquid phase even at the lowest temperature practically obtainable. Condensation for air pollution control is generally used as a pretreatment to reduce the load on a more efficient process such as adsorption or incineration.

(5) Control by Substitution of Materials:

Changing the process so that no solvent is needed or switching to an aqueous solvent or an organic solvent that is less odorous. In

general, however, this approach is more attractive on paper than it is in practice, because of the difficulty in obtaining a water-thinned or solvent free product that will give adequate on-the-job performance. The substitution of photochemically nonreactive materials as a stationary source control measure has been largely limited to solvents used in degreasing operations, in surface coatings and in printing inks(6). In some cases, satisfactory reformulation of products with nonreactive solvents has not been achievable, and in other cases the increased costs are greater than those for control equipment.

(6) Flaring:

Flares are preferred when disposing of gas streams with sufficient heat value to attain the combustion temperature without the use of supplemental fuel. Flares are also preferred when disposing of gases with little recovery value, or for gases containing contaminants that make recovery unprofitable. Not all of the organics are completely oxidized to carbon dioxide and water. As much as 10 percent of the combustion products may be carbon monoxide. Materials that cause health hazards or nuisances should not be combusted in flares. Compounds such as chlorinated hydrocarbons require special combustion products.

(7) Absorption

Absorption is another air cleaning process that is used primarily for gaseous contaminants. In an absorption process,

also referred to as "gas scrubbing" or "air washing", an air stream contaminated with a gaseous pollutant is brought into contact with a washing liquid and the pollutant is dissolved into the solution. Typically, the contaminated air is passed through a liquid spray or over the wetted surfaces of a media. The pollutant is absorbed from the air only if it is soluble in the liquid and a driving force exists for transfer of the pollutant from the air to the liquid. To prevent saturation of the washing liquid with the pollutant and, thus, to maintain a driving force for pollutant transfer, the washing liquid must be periodically or continuously replaced or regenerated(7).

The washing liquid to be employed for this air scrubbing depends on the gaseous pollutant to be removed. A primary criterion for choosing a washing liquid is the solubility of the gas in the liquid. The pollutant solubility should be high.

Air washing is frequently employed for removing pollutants from industrial contaminated-gas streams and, consequently, equipment is commercially available(7).

Since the aim of this thesis is to provide an efficient absorption technique, It will be discussing this more thoroughly in the following paragraphs.

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B. Previous work and Principles of organic vapor absorption

Effluent gases can be scrubbed absorbed with a suitable liquid to remove the organics. This approach is especially attractive where it can be employed. Every working day, millions of cubic feet of industrial air are cleansed of hundreds of tons particulate and contaminant gases using wet scrubbers(7). These specially designed scrubbing systems prevent contaminants from attaining levels which may be injurious to people, plant and animal life, and the environment.

Organic vapor absorption is an operation in which a organic vapor mixture is contacted with a liquid for the purposes of preferentially dissolving one or more components of the organic vapor and to provide a solution of these in the liquid(8).

The two basic factors controlling the gas absorption process are
(1) The degree of solubility of the gas to be removed in the liquid used for scrubbing.
(2) The means of obtaining intimate contact between the gas and liquid streams to bring about the quickest absorption rate possible.

Operation of organic vapor absorption require mass transfer of a substance from the organic vapor to the liquid. The rate of

absorption depends upon the departure from equilibrium conditions, and it is therefore necessary to consider the equilibrium of vapor-liquid systems. The scrubbing of solvent vapors from an air stream depends on the equilibrium concentrations of the solvent in the gases and the liquid phase.

If a quantity of a organic vapor and a relatively nonvolatile liquid are brought to equilibrium, the resulting concentration of dissolved vapor in the liquid is said to be the gas solubility at the prevailing temperature and pressure. If a mixture of organic vapor is brought into contact with a liquid, under certain conditions, the equilibrium solubilities of each organic vapor will be independent of the others, provided, however, that the equilibrium is described in terms of the partial pressures in the organic vapor mixture. The solubility of a organic vapor will be influenced by the presence of a nonvolatile solute in the liquid.

Those organic compounds which are normally immiscible or partly miscible in water can be gas contaminants, the subsequent removal of these gases from an air stream by a liquid medium is dependent on their solubility in the medium. Water, the most economical liquid scrubbing medium by far, is usually examined first for possible use(9). It is generally considered impractical to collect water immiscible organic compounds from the vapor phase in water with a high degree of efficiency. One of the principal reasons for this has been the organic compound is high vapor pressure or partial pressure contribution to the gas phase of the

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system once equilibrium has been reached. Non polar organics in water tend to exhibit higher vapor pressures than when pure in water due to their high activity coefficients.

Immiscibility and therefore the solubility of one compound in another is a function of the physical properties of the solute-solvent interface. Bonilla and Baron studied the absorption of ethylene oxide in a packed column with various aqueous and non-aqueous solvents. They varied the gas temperature and concentration in the air stream and concluded that the liquid-film resistance is the controlling factor for absorption, providing there is some degree of solubility.

Othmer and Scheibel(10) in doing work with acetone in a semi-commercial packed tower; varied the range of concentration of acetone in the air and in the washing solutions. They found the rate of acetone absorption was dependent on both the liquid and gas films. Interfacial resistance seems to be the governing factor determining mass transfer and mass transfer rates.

Rate of absorption of a solute from a gas by a liquid is limited by processes of diffusion which occurs from the high concentration region of the solution to one of low. Molecular diffusion is concerned with the movement of individual molecules through a substance by virtue of their thermal energy. In the case of simplified kinetic theory a molecule is imagined to travel in a straight line at a uniform velocity until it colloids with

another molecule, whereupon its velocity changes both in magnitude and direction. The molecule travels a highly zigzag path, and the net distance in one direction which it moves in a given time, the rate of diffusion is only a small fraction of its actual path. As opposed to molecular diffusion which is a slow process, the method of solute transfer brought about by mechanical agitation is known as eddy or turbulent diffusion.

In discussing the principles of gas absorption, Lewis and Whitman(11)(12) also tell us that when a liquid and gas come in contact, there are film layers between them. On the gas side as well as the liquid side of the interface there is a film layer in which motion by convection is slight. Therefore, the transfer of solute through the films is by slow diffusion and they are the controlling parameters of absorption. They devised the following equation pertaining to absorption:

Rate of absorption = dw / Adt = Kg(Pg - Pi) - Ki(Ci - Cl)

w -- weight of solute (grams)

t -- time (hours)

P -- concentration of solute in gas (atmosphere)

g -- outside gas film

i -- interface

l -- inside liquid film

Lewis and Whitman further explain that mixing increases the interfacial area between the gas and liquid and from this standpoint alone absorption increases.

Confirming this work, Donnan and Masson(13) in formulating their theory of gas scrubbing towers with internal packing, have come up with the following criteria for higher absorption efficiency:

a) The interfacial area between the gas and washing liquid must be large.

b) There must be a high relative motion between gas and liquid.

c) There must be a degree of turbulent motion in one or both phases.

d) There must be a sufficient rate of flooding to obtain the maximum drip effect.

Mixing obviously accomplishes the first three criteria and should increase absorption.

However, as was seen previously, absorption is controlled by the physical properties of the media involved, and in order to have and absorption rate to influence, one must first have absorption. V. Koran(14) studied the action of vapors of some organic liquids on the surface tension of water. The surface tension varied over the range or organics used, but it was found that the surface activity of these vapors and their effect on water parallel the interfacial activity of the corresponding organic liquid phases upon water.

Schwartz and Perry(15) explain that most organic compounds which are soluble in water lower its surface tension.

Brown's fundamental principle(16) governing the process of gas

washing for the recovery or removal of a gas or vapor component is that the scrubbing liquid can absorb the gas or vapor until the vapor pressure of the latter in solution is equal to the partial pressure of the gas or vapor in the gases entering the washing unit.

Summarizing the previous work cited on absorption, and our main interest in absorption of gases in scrubbing, we find that Baker(17) has defined the absorption of a gas from a gas mixture by a liquid as a product of five factors:

1) The theoretical absorption -- the vapor pressure of a gas in a liquid phase equals the partial pressure of the gas in the gaseous phase. The liquid will be saturated with gas when the absorbed gas exerts no pressure.

2) The difference in these partial and vapor pressures -- this difference is the force which determines rate of absorption and will not equal zero in commercial work.

3) The intimacy of contact of gas and liquid phases.

4) Contact time of gas and liquid phases.

5) A proportionally constant that depends on the units in which the other factors are expressed.

The scrubbing of organic insoluble vapors in water seems impractical. Further work in the area was done by Cutting and Jones(18), who studied the effect on the surface tension of water of various vapor pressures up to saturation of immiscible organics. They found that in all cases at low vapor pressures the surface tension decreases almost linearly with increasing vapor

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pressure, whereas at higher vapor pressures the change in vapor pressure increases continuously with pressure. We therefore realize the surface tension of water can be affected by organics to some extent to allow for greater absorption.

Surface active agents have different properties from that of water; they are organic compounds, and like most organic compounds they lower the surface tension of the solvent/solute system. Mirev, Elenkov, and Balarev(19) have done much work with absorption and surface-active agents. Through their experiments, we realize that surface active agents work to allow or increase absorption.

C. Surfactant and solubilization effects

Surface-active agents (or, more briefly, surfactants) are used extensively in industrial application for product formulation, process control, particle size control, and surface modification(20). In the field of pollution control, however, surfactants are generally the cause of problems because the stability of surfactants which cause environmental pollution(21).

In recent years the effect of surfactants on gas absorption has received increasing attention for various reasons. Surfactant-Based separation processes are a major emerging technological area in both surfactant science and separations science. Surfactant-based separations have a number of potential advan-

tages over traditional methods. They are often low-energy processes because large temperature or endothermic phase changes are not being used to effect separations. Surfactants are often environmentally innocuous and low toxicity, so that the leakage of a small concentration of surfactant into an aqueous process stream from the separation may be tolerable, in contrast to other air pollution control techniques. It also provides a cost-effective, viable solution to a major air pollution problem.

Applications of surfactant-based separations must be treated mildly. Pollution control of water and air streams can be done effectively with surfactant technology which shows great potential for removal of organics or scrubbing volatile organic compounds from air(22).

The groups of chemical compounds known as surfactants are, in the most common form, constructed of a hydrocarbon portion and a polar or ionic portion as illustrated schematically in Fig. 1.(23) the hydrocarbon portion, which can be linear or branched, interacts only very weakly with the water molecules in an aqueous environment. Moreover, the strong interactions between the water molecules arising from dispersion forces and hydrogen bonding act cooperatively to squeeze the hydrocarbon out of the water, hence the chain is usually called hydrophobic. The polar or ionic portion of the molecule, usually termed the head-group, however interacts strongly with the water via dipole-dipole or ion-dipole

interactions and is solvated. Consequently the head-group is said to be hydrophilic(23).

Chain   Head

Linear   or   Branched   Group

Hydrocarbon   or   Fluorocarbon
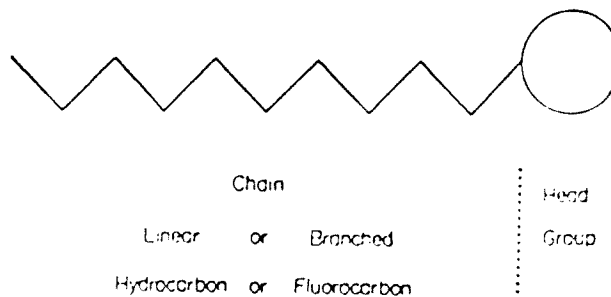
Fig.1-1. Schematic diagram of surface active molecule.

It is essentially the balance between the hydrophobic and hydrophilic parts of the molecule or ion in solution which gives the special properties which we associate with surface active agents. In addition to the name surface active agents these materials are often called by other names which include:

surfactants (particularly in the USA);

association   colloids;

colloidal   electrolytes;

paraffin   chain   salts;

amphipathic compounds;

tensides (particularly in Europe).

A surface-active agent is a substance that has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). The interface indicates a boundary between any two immiscible phases; the term

surface denotes an interface where one phase is a gas, usually air.

A interfacial free energy is the minimum amount of work required to create that interface. The interfacial free energy per unit area is what we measure when we determine the inter facial tension between two phases. It is the minimum amount of work required to create unit area of the interface or to expand it's unit area. When we measure the surface tension of a liquid, we are measuring the interfacial free energy per unit area of the boundary between the liquid and the air above it.

Surface-active agents have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyophoic group (or polar portion), together with a group that has strong attraction for the solvent, called the lyophilic group (or hydrocarbon portion). This is known as an amphipathic structure. When a surface-active agent is dissolved in a solvent, the presence of the lyophobic group in the interior of the solvent causes a distortion of the solvent liquid structure, increasing the free energy of the system. In an aqueous solution of a surfactant this distortion of the water by the lyophobic (hydrophobic) group of the surfactant, and the resulting increase in the free energy of the system when it is dissolved, means that less work is needed to bring a surfactant molecule than a water molecule to the surface. The surfactant

therefore concentrates at the surface. Since less work is now needed to bring molecules to the surface, the presence of surfactant decreases the work needed to create unit area of surface (the surface free energy or surface tension). On the other hand, the presence of the lyophilic (hydrophilic) group prevents the surfactant from being expelled completely from the solvent as a separate phase, since that would require desolvation of the hydrophilic group. The amphipathic structure of the surfactant at the surface and reduction of the surface tension of the solvent, but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it. A surface-active agent is therefore a substance that adsorbs at some or all of the interfaces in the system and significantly changes the amount of work required to expand those interfaces. Surfactants usually act to reduce interfacial free energy rather than to increase it, although there are occasions when they are used to increase it.

When the phase boundary area of so large relative to the volume of the system that a substantial fraction of the total mass of the system is present at boundaries (e.g., in dispersions of all sorts, such as emulsions, colloids), surfactants can always be expected to play a major role in the system(24). When the phenomena occurring at phase boundaries are so unusual relative to the expected bulk phase interactions that the entire behavior of the system is determined by interfacial processes (e.g., hetero-

geneous catalysis, corrosion, detergency, or flotation), surface-active agents can play an important role in the process.

The molecules at a surface have higher potential energies than those in the interior. This is because they interact more strongly with the molecules in the interior of the substance than they do with the widely spaced gas molecules above it. Work is therefore required to bring a molecule from the interior to the surface.

The absorption of solutes leads to changes in the surface tension compared with that of the pure solvent. The change in surface tension with increasing concentration of solute is given by the famous Gibbs adsorption theorem(25):

$$dr = - SsdT - T1du1 - ... -Tidui$$

where dr of the differential of the surface tension and Ss is the excess entropy of the surface, i.e. is the difference between the entropy of the real system and that of a hypothetical system in which the concentration of each species in each phase remains constant up to the physical boundary of separation between the liquid and vapor phases. Excess free energy and excess enthalpy of the system are similarly defined and are frequently referred to as the surface free energy and the surface free enthalpy respectively.

T1,..., Ti are the surface excesses of the absorbed compo-
nents, 1,2,3,...,i, and du1,...,dui are the differentials of the
chemical potentials of the components 1,2,3,...,i.

If the surface tension falls with increasing concentration,
absorption of the solute is positive, it also occur the surface
tension rises with increasing concentration. The latter occurs
with solutions of many simple inorganic salts, the possible range
of increase of surface tension being limited to only a few dynes
per centimeter. Positive adsorption occurs very commonly with
solutions of organic substances.

Surface activity depends on the structure of the surfactant,
and the solvent, temperature, and other conditions of use.

From the previous work we could conclude that immiscible organ-
ic compounds can be recovered from an air stream by the use of
surfactants modifying the solubility of scrubbing liquid.

II. EXPERIMENT

A. EQUIPMENT AND MATERIALS

Equipment

Isothermal vapor-liquid equilibrium experiments were performed with sealed vials placed into an ultrasonic bath of dimensions 15 x 14 and 9.5 cm deep and power of 55 watts. The constant temperature bath apparatus(Figure II-1 and II-2) consists of a instant immersion heater(TAIWAN, 45v, 300 W), an ultrasonic bath and a temperature controller. Temperature was measured by a thermocouple and controlled by a constant temperature controller (OMEGA ENGINEERING INC.) When a temperature, (e.g. 40 C), is set on temperature controller, the heater would start to increase the temperature in the bath. The thermocouple/controller monitors the temperature in the bath and maintains it at the desired setting. The bath water volume is about 1470 CM^3. Temperature was read with ± 1.0 accuracy.

Samples were analyzed in a gas chromatograph (26) (Perkin-Elmer 3920 B) equipped with flame ionization detector. The chromatographic column was 4 meters of 0.125-inch (OD) stainless steel tubing, packed with 3% SP - 2250 on 100/200 SUPELCOPORT. The column was connected to the instrument inlet and detector

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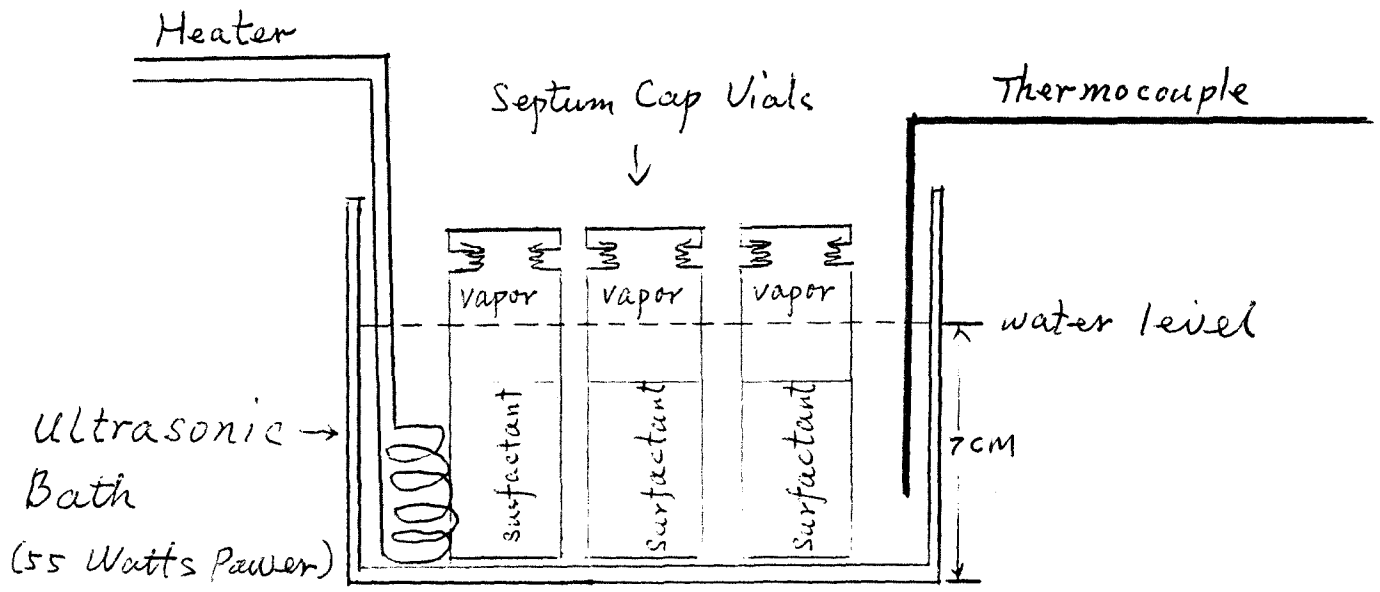
Fig.II-1 Side View of the Constant Temperature Bath Apparatus

⬭ Vials   ⓔ Heater   ● Thermocouple
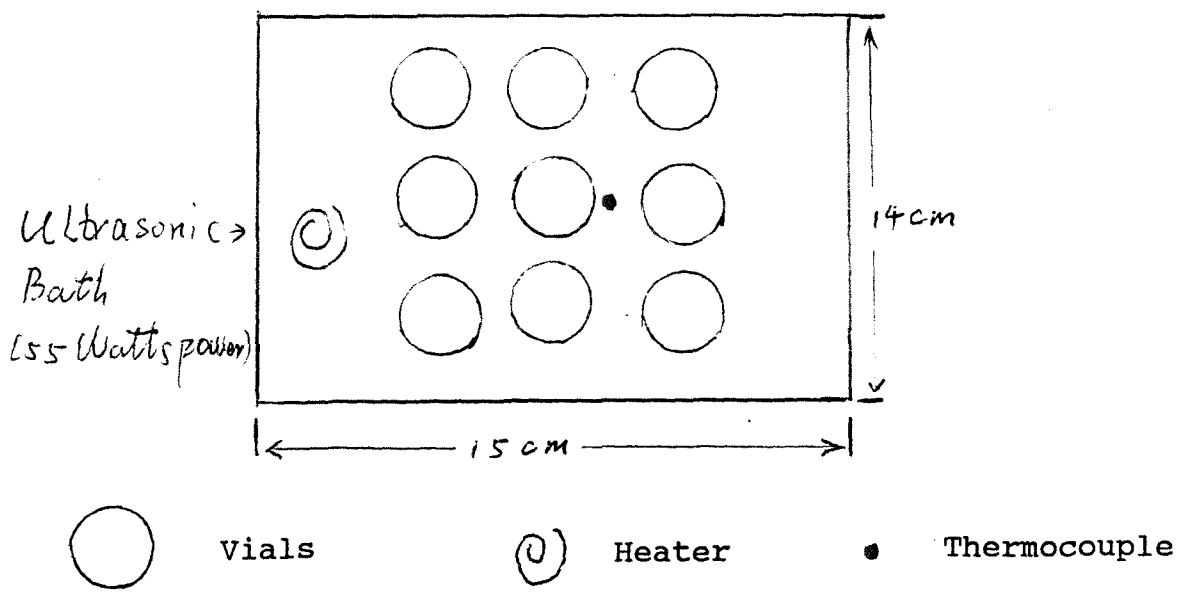
Fig.II-2 Top View of the Constant Temperature Bath Apparatus

with stainless steel tubing connectors and ferrules. Splitless injector is used with thermogreen LB-2 septa, 9.5 mm (3/8") (SUPELCO Inc,). The syringe used for standard injection is regular liquid 10 ul syringe (UNIMETRICS CORPORATION). The syringe used for vapor sample injection is regular 0.5 ml syringe for liquid samples (B-D GLSPAK).

Nitrogen gas (Liquid Carbonic, Specialty Gas Corporation, Harrison, NJ) flow through the column was 30ml/min. measured by a rotameter, with the entire effluent passing into a flame ionization detector which was used for quantifying the organic compounds (non oxygenated and non chlorinated). The other gases to the flame ionization detector are hydrogen (30 ml/min.) and air (300ml/min.) The column was operated isothermally at approximately 110 C. The chromatograph also had a short precolumn which protect contamination from the main column. The inlet temperature was set at 125 C. The detector temperatures were set at 270 C. The column was routinely baked out overnight at 120 C and a constant, low-level baseline at the most sensitive setting obtained. The instrument was calibrated with standard solutions of the organic solvents in acetone or in toluene.

The signals of the eluted compounds are collected and the peak area are calculated by an computer integrator (SP4290, Spectra-Physics, San Jose, CA). The following conditions were set up on

the integrator and were held constant throughout our tests:

Chart speed -- 0.5 inch / min.

Chart span -- 1.0 mv(full scale)

The attenuator setting was varied depending on the organic compound's individual response and the sample size.

For each organic compound tested, the sample size was coupled with the setting which provided the optimum results. For example the attenuation was set on 8 for Acetone when 0.2ml vapor samples were injected.

The gas chromatograph detector output was connected to a printing computer integrator. The vapor phase organic level was read from a calibration curve. The calibration curve was made by plotting in expanded coordinates the peak area of each pure organic solvent vs. its known number of moles. These were prepared by weight and converted to moles with the known molecular weight.

Materials

The acetone and the toluene were obtained from American Burdick & Jackson Co. and Baxter Healthcare Corporation. The butyl acetate, i-propanol and methyl ethyl ketone were obtained from Fisher Scientific Co.Springfield, NJ. All organic solvents were used as received without further purification. Some of the solvent parameter at 20 C are listed in Table I. Some physical constant of the solvents are listed in Table II.

Table II-1. Physical properties of organic solvents at 20 C

Solvent	Dipole moment Debye	Molecular parachor*	Electronic polarization Pe
Toluene	0.4	244	30.9
Isopropanol	1.7	165	17.6
Butyl acetate	1.8	295	31.6
Acetone	2.9	162	16.1
Methyl ethyl ketone (2-butanone)	2.8	199	20.8

* molecular parachor: an empirical constant for a liquid that relates the surface tension to the molecular volume. This may be used for a comparison of molecular volumes under conditions such that the liquids have the same surface tension and for determination of partial structure of compounds by adding values obtained for constituent atoms and structural features called also molar parachor, molecular parachor(27)

Table II-2. Physical constant of the organics

Solvent	Formula	Molecular Weight (gm/mole)	Boiling point(C)	Density(28) (gm/ml at 20 C)
Toluene	C6H5-CH3	92.13	110.6	0.8669
Isopropanol	CH3CH(OH)CH3	60.11	82.4	0.7855
Butyl Acetate	CH3CO2(CH2)3CH3	116.16	126.5	0.8825
Acetone	CH3COCH3	58.08	56.2	0.7908
Methyl ethyl ketone (2-Butanone)	CH3CH2COCH3	72.12	79.6	0.8054

Octylphenyl-decahydroxylate(OPD) and Sorbitan Monooleate(SM trade name: Span 80) were obtained from ICI Americas Inc.. Sodium Sulfonate (SS) was obtained from Witco Chemical Corporation. The surfactants employed in this experiment were used as received without further purification. The molecular weight and density of surfactants are listed in Table II-3.

Table II-3.   Physical Constants of Surfactants

Surfactant	Molecular Weight	Density
OPD	624	1.050
S M	450	1.031
S S	471	1.036

Sodium sulfonate (or sodium petroleum sulfonates) are mixtures obtained by treating high-boiling petroleum fractions with oleum, sulfur trioxides, or sulfuric acid, followed by neutralization. The major active substances are the salts of high-molecular-weight sulfonic acids. The sulfonic acid moiety is attached, for the most part, to a carbon atom of the aromatic ring. A minor amount of the aliphatic and alicyclic hydrocarbons present in the petroleum fraction are, in addition sulfonated under the same conditions. Thus, petroleum sulfonates are a complex mixture of different molecules. They are the hydrocarbon oils which has not reacted and contain aliphatic and alicyclic, particularly naphthenic, hydrocarbons. Table 4 shows the properties of sodium salts.

B. Experimental Procedure

a. Standard preparation analysis

a.1 Make up of standard

The pure solvents of each analyte of interest: acetone, toluene, butyl acetate, i-propanol and methyl ethyl ketone are used for standard calibration curves respectively. The solvents are diluted by Toluene (MEK, i-Propanol and Acetone) and Acetone (Toluene, Butyl Acetate) to 3-5 specific concentrations. For example: Toluene is diluted to concentrations of 0.4%, 0.8%, 1.2%, 1.6%, and 2.0% in Acetone. These liquid standards are injected into the gas chromatograph 1.0 ul liquid to establish a linear response over the range of the sample concentrations of the vapors(see Table II-5). The concentrations correspond to the expected range of vapor levels found in samples of the vapor/liquid equilibrium experiments.

Table II-5. Concentration of Organic Standards

Standards	Diluted Concentration (%)				
MEK	0.5	1.0	1.5	2.0	2.5
Toluene	0.4	0.8	1.2	1.6	2.0
Butyl Acetate	1.0	1.5	2.0	2.5	3.0
Acetone	0.5	1.0	1.5	2.0	2.5
i-Propanol	0.5	1.0	1.5	2.0	2.5

Standards are injected as liquids (1.0 ul) with 10 ul regular liquid syringe(UNIMETRICS CORPORATION). Each calibration standard is injected using the a similar technique to that which is used to introduce the actual vapor samples into the gas chromatograph. Tabulate peak area responses against the mass injected. The results are used to prepare a calibration curve for each analyte.

The working calibration curve is verified on each of experiments day by the injection of one calibration standard. The flame ionization detector requires less frequent verification, because it is less sensitive than other detectors, such as electron

capture that operate in the sub-nanogram ranges and are more susceptible to changes in detector response caused by GC column bleed and sample effects. If the response for every analyte varies from the predicted response by less than ± 15%, the old calibration curve is utilized. New standard curves were make up 3 times over the one year of the project.

The concentration of each analyte in the sample is determined by calculating the amount of standard injected from the peak response, using the calibration curve (Standard curves are shown in the next section).

b. Sample preparation

The 40ml vial was weighed with cap and label(W_1). Approximately 20ml surfactant (octylphenyl-decaethoxylate, sorbitan monooleate or sodium sulfonate) was placed into the 40ml vial and was weighed(W_2). The weight of surfactant equals W_2 minus W_1. Then, approximately 1%, 2%, 4% and 8% the of surfactant weight of organic solvent (Acetone, Toluene, Butyl Acetate, i-Propanol or Methyl- ethyl Ketone) was added to the vial and weighed (W_3). The weight of solvent results from W_3 minus W_2. The vials with the Teflon-lined screw cap were sealed with a neoprene septum and shaken vigorously for 5 min.

c. Isothermal vapor-liquid equilibrium

The isothermal vapor-liquid equilibrium was determined at 4 different temperatures, room temperature (21 C to 24 C), 40 C,

60 C and 70 C. For room temperature, the sample vial was placed at room temperature 24hrs to reach the equilibrium state after it was mixed well by ultrasonic. For the other temperatures, the sample vial was set into an ultrasonic bath at 40 C, 60 C or 70 C (water bath) respectively for not less than 30 min. where temperature was maintained by a heater and a temperature controller in a ultrasonic bath.

The vapor pressure of a gas in a liquid phase equals the partial pressure of the gas in the gaseous phase upon saturation of the liquid. The partial pressure of the gas decreases as the vapor pressure increases until equilibrium is achieved in a closed system. The closed system is our 40 ml vial. we note this reduction in partial pressure results in a reduction in concentration of the organic compound in the vapor phase. This is also the increasing of its concentration in the surfactant- organic solvent mixture; increasing the amount of organic absorbed in the surfactant which leads to the solubility of the organic in the system.

d. Analysis of sample

The vapor samples were withdrawn by syringe through the septa and injected directly into the gas chromatograph to determine the organic compound concentration in the vapor. A 0.5 ml syringe(B-D GLASPAK) was used for vapor sample injection. The sample size ranged from 0.1 ml to 0.5 ml, depending on the

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organic compound's response with the gas chromatograph. The GC column is kept at 110 C isothermally. It takes approximately 10 minutes for a sample to elute the column.

TABLE II-4

Typical Properties of Oil-Soluble Sodium Petroleum Sulfonates [29]

Properties	Low-molecular-weight products	Medium-molecular-weight products	High-molecular-weight products	Very high-molecular-weight products	80% active conc. product
Sodium sulfonate, %	62-65	60-62	61-62	62	80
Equiv. wt.	410-430	440-470	490-510	560-580	405-420
Mineral oil, %	30-35	32-36	32-33	32-33	11
Water, %	1.5-4.5	2-5	4-5	5	8
Inorganic salts, %	0.5	0.5	0.5	0.5	0.7
Color, ASTM D1500	2.5-4	2-5	5	4	2
Furol viscosity at 210° F	110-125	125-140	175	100	200

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III. DATA ANALYSIS PROCEDURE

A. Standards

a. Plot Peak Area vs ul of standard injected

The peak area of each different concentration standard obtained from the integrater was plotted against the microliter(s) of the standard injected into the gas chromatograph.

b. Establish linear response within the range of the samples.

When we obtain above graph, we decide range of the vapor sample concentration in the graph and use this range in standard curve for vapor sample.

c. Calculate the conversion factor

The volume of the standard injected is converted into the moles of each standard which serve as a horizontal axis of the calibration curve of each analyte of interest. The conversion factor is calculated as follow:

$$\frac{\text{injected volume(ul)/ dilution factor} * \text{specific gravity(g/ml)}}{\text{molecular weight(gm/mole)} * 1000}$$

= gm-moles

Example:

methyl ethyl ketone: inject volume: 0.5ul

                        dilution factor: 20

                        specific gravity: 0.805 g/ml

                        molecular weight: 72.10 g/mole

The g moles of methyl ethyl ketone would be:

$$\frac{0.5 \ (ul) \ / \ 20 \ * \ 0.805 \ (g/ml)}{72.10 \ (g/mole) \ * \ 1000 \ (ul/ml)} = 2.79 \ * \ E\text{-}07 \ g \ mole$$

we obtain the standard curve of each analyte of interest by plotting the peak area vs. the moles of standard (see Fig. III--1, III--2, III--3, III--4 and III--5).

B. Sample Data

a. Normalized peak area for vapor mole fractions of different sample injected volumes.

The sample volume injected is not constant, because of varied concentrations in vapor phase relative to the desired range of peak height on the chromatogram. To calculate the mole fraction in vapor phase, we need to account for this nonuniform sample injection volume. Before the calculation of the mole fraction in

vapor phase, the peak area of the sample volume should be normal-
ized. An example follows:

If I wish to use 0.3ml as the calculation volume, and 0.5ml is
the injected volume then this is normalized by :

$$\frac{\text{peak area of 0.5ml injection} * 0.3}{0.5} = \text{peak area of 0.3ml injection}$$

b. calculate the mole fraction in vapor phase

$$\text{The mole fraction in vapor phase} = \frac{\text{g mole of sample in vapor phase } (N_i)}{\text{g mole of total gas molecules in vapor phase} (N_t)}$$

The value of N_i is obtained from the experiment and the equa-
tion which characterizes calibration curve of each analyte.

The value of N_t is obtained from :

$$P V = n R T$$
$$n = P V / R T$$

P: 1 atmosphere

V: the normalized inject volume (ml)

R: 82.06 (cm^3 atm/OK-mole)

T: The room temperature during the experiment (C) + 273 (the
syringe injecting the sample was at room temperature)

If I used the 0.3ml as the injection volume while room
temperature is 21 C, the N_t should be:

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$$N_t = \frac{1 * 0.3(ml)}{82.06 * (21 + 273)} = 1.24 * E\text{-}05 \ (moles/cm^3)$$

c. calculate the mole fraction in liquid phase

The mole fraction in liquid phase equals the g mole of organic solvent in liquid (N_s) over the total g-moles (solvent + surfactant N_t) including the solvent and surfactant ($N_{surf.}$). Calculation of N_s of Methyl Ethyl Ketone:

$$N_s = \frac{W_3 - W_2 (= gms \ solvent)}{molecular \ weight \ of \ the \ solvent}$$

eg: W_3 : 47.97 g

W_2 : 47.65 g

MW : 72.10 g (Methyl Ethyl Ketone)

$$N_s = \frac{47.97g - 47.65g}{72.10 \ g/mole} = 4.44E\text{-}03 \ g \ mole$$

N_t is a sum of N_s plus $N_{surf.}$

$$N_{surf.} = \frac{W_2 - W_1 \ (\ weight \ of \ surfactant \ )}{M \ W \ (\ molecular \ weight \ of \ surfactant \ )}$$

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eg: $W_2 - W_1$: 22.42 g

M W   : 624 g (Octylphenyl Decaethoxylate)

$N_{surf.} = 22.42 / 624 = 3.59E-02$

then we have the N_t:

$N_t = N_{surf.} + N_s = 3.59E-02 + 4.44E-03 = 4.04E-02$

Now, we have the parameters needed for calculating the mole
fraction in liquid phase.

$$\text{The mole fraction in liquid phase} = \frac{N_s}{N_{surf.} + N_s} = \frac{N_s}{N_t} = \frac{4.44E-03}{4.04E-02}$$

$$= 1.10E-01$$

d. Plotting the mole fraction distribution curve

Plotting the mole fraction in vapor phase vs. the mole frac-
tion in liquid phase, we gain the Henry's law plots of each
organic solvent in the three different surfactants at each of
the four different temperatures.

e. Precision

The analysis precision was calculated as percent relative standard deviation. The experimental determined standard deviation for analyses of vapor samples is 1% of vapor mole fraction by 2-3 injections, and C.V.% is 3.7%.

f. Calculation of Henry's law constants

Henry's law in terms of partial pressure is as follow(29):

$$P_i = He \ A^*$$

P_i: the partial pressure of the gas over the liquid.

He: Henry's law constant.

A^*: the concentration of dissolved gas in liquid when it is
   equilibrium.

thereby we can obtain the He:

$$He = P_i \ / \ A^*$$

in this experiment, Henry's law constant equals the partial pressure(P_i) of each organic above surfactant over the concentration(A^*) of dissolved gas in surfactant.

P_i(atm): the organic vapor mole fraction times 1 atmosphere(the
            unit we choose).

A^*(mole/liter): the mole(s) of organics per liter surfactant.

Because we need the volume of the surfactant to calculate the A^*, we obtain it by using the mass of the surfactants which we already have listed in previous data and the density.

ml Surfactant = Surfactant(gm) / Density surfactant(gm/ml)

For example:

At 22 C, the organic vapor mole fraction of Acetone over Octylphenyl Decaethoxylate is 1.1E-02; the mole(s) of Acetone in Octylphenyl Decaethoxylate is 4.8E-03; the weight of this surfactant is 24.39gm; density of the surfactant is 1.05gm/ml. Used these parameters, we obtain the volume of Octylphenyl Decaethoxylate and A^* as follow:

Surfactant(ml) = 24.39(gm) / 1.05(gm/ml) = 23.23(ml)

A^* = 4.8E-03(mole) x 1000(ml/liter) / 23.23(ml)

    = 2.1E-01(mole/liter)

P_i = 1.1E-02 x 1 (atm) =1.1E-02(atm)

then:

He   = P_i / A^* = 1.1E-02(atm) / 2.1E-01(mole/liter)

    = 5.2E-02(atm)(liter) / mole

Henry's law constants of five organics in the three surfactant over all temperatures and liquid concentration ranges are listed in tables IV-1 to IV-6.

Fig.III--1 STANDARD CURVE (FID-GC)
Methyl Ethyl Ketone
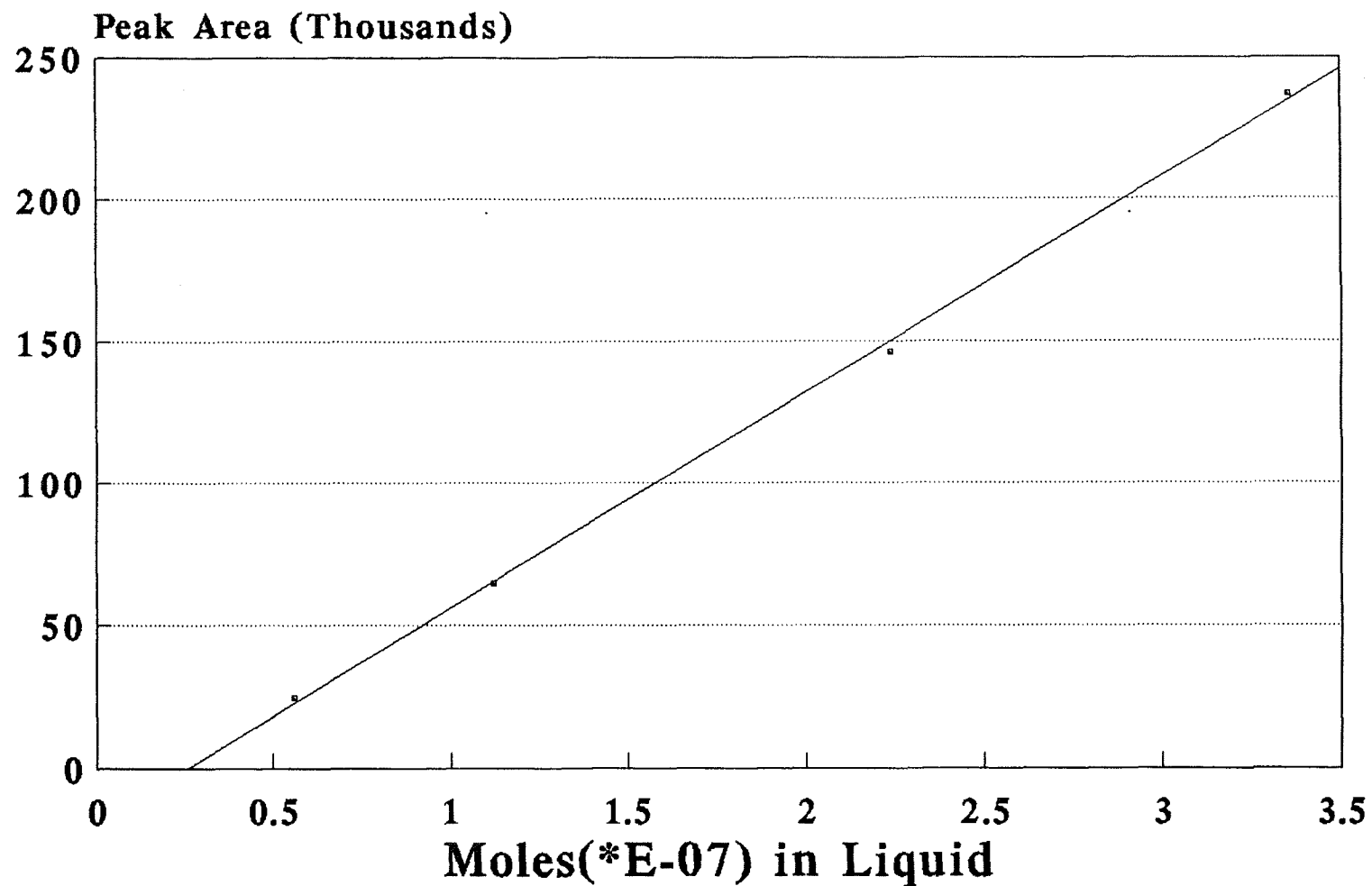
Fig.III--2 STANDARD CURVE (FID-GC)
Toluene
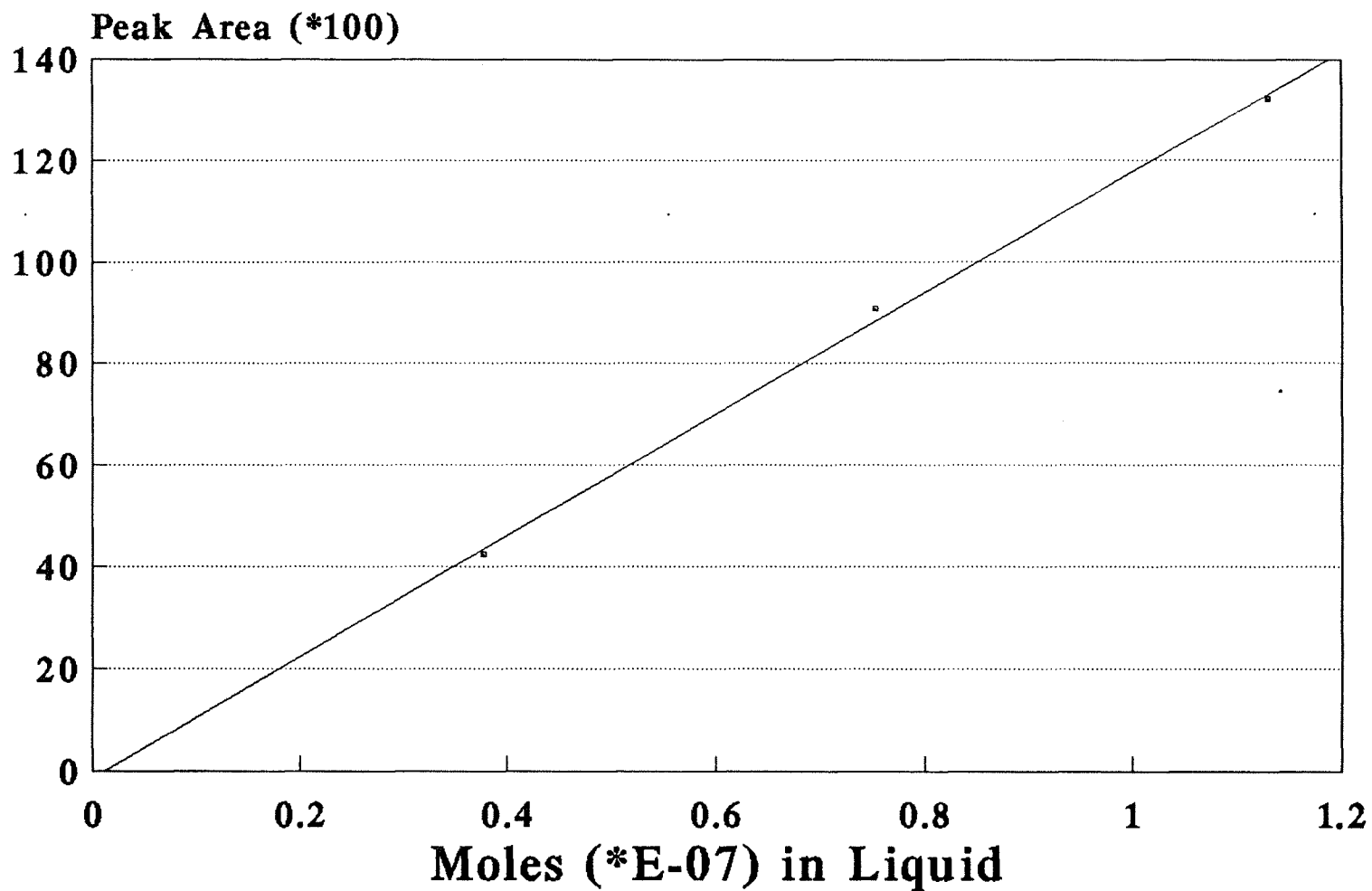
Fig.III--3 STANDARD CURVE (FID-GC)
Butyl Acetate

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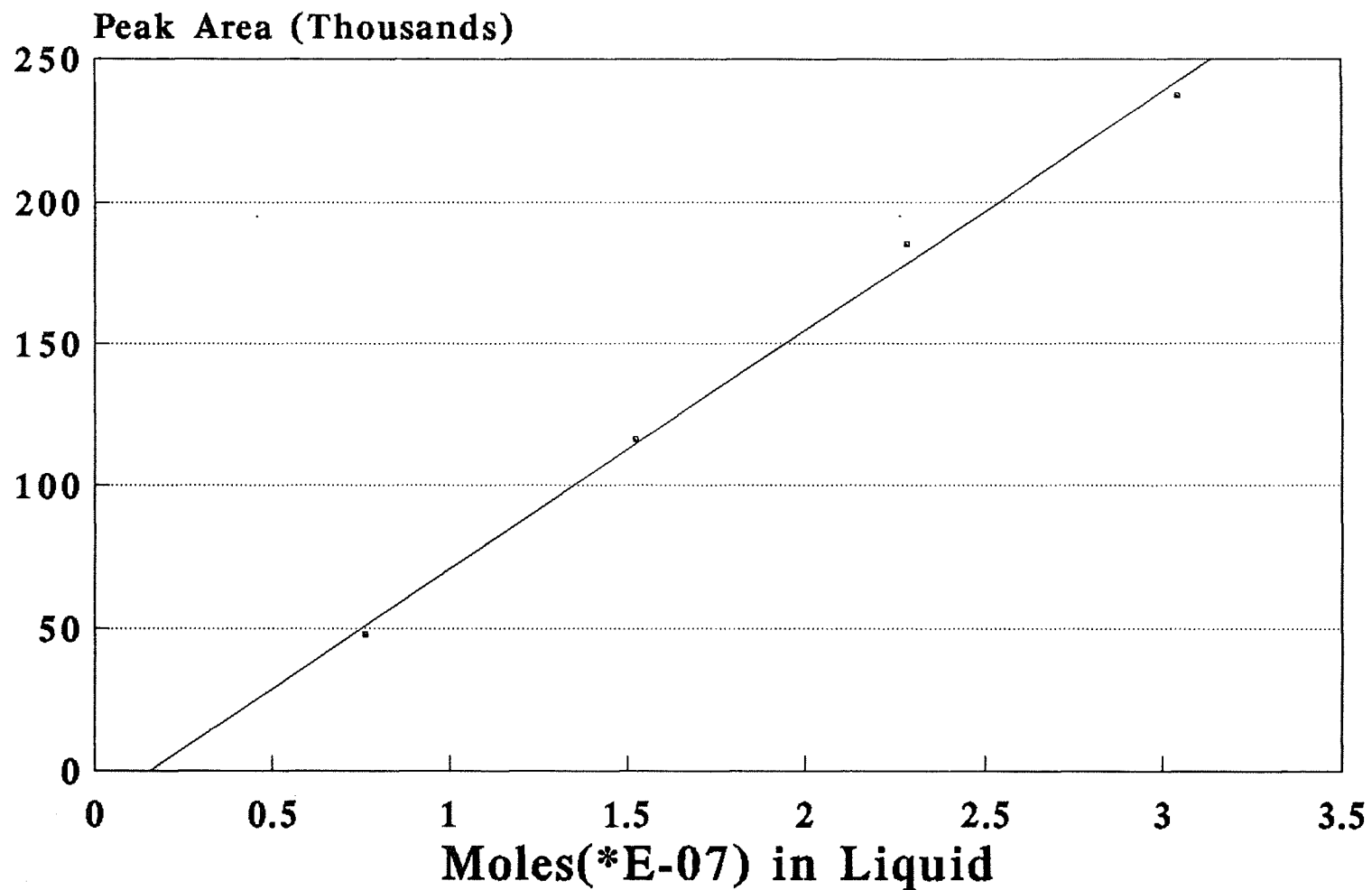
Fig.III--4 STANDARD CURVE (FID-GC)
Acetone

44
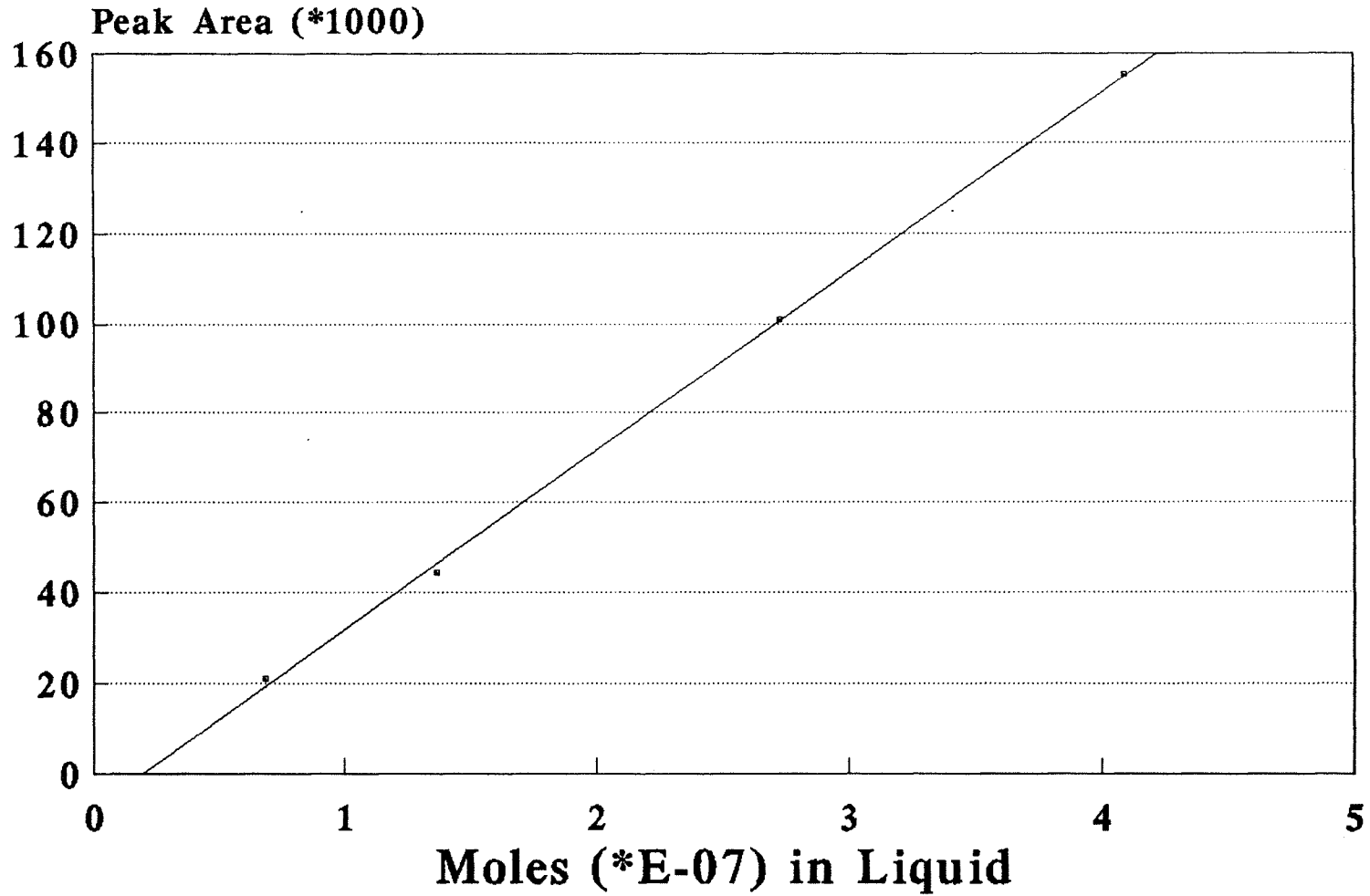
Fig.III--5 STANDARD CURVE (FID-GC)
i-Propanol
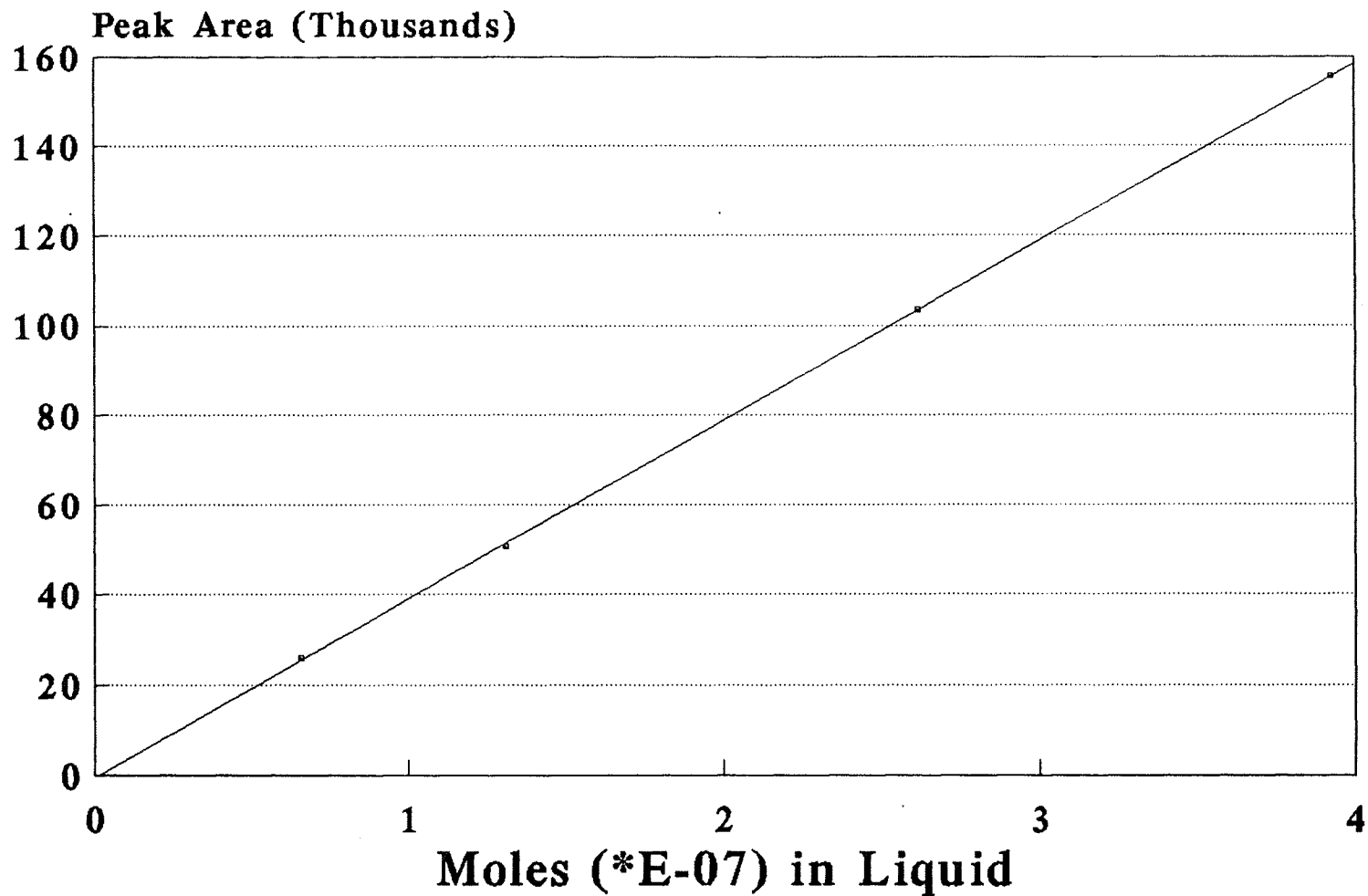
IV. RESULTS AND DISCUSSION

Three surfactants are used in a study to determine effective-
ness for scrubbing of volatile organics normally considered
immiscible or partly miscible in water solutions (organics from
an air stream here). The scrubbing liquids we studied are the
pure surfactants. The surfactants which we used in this experi-
ment are shown to have specific capabilities for the absorption
of volatile organics. These experiments provide quantitative data
on these effects.

The study consisted of experiments with five volatile organics:

-- Acetone

-- Toluene

-- Methyl ethyl ketone (MEK)

-- isopropanol (i-PrOH)

-- n-butyl acetate (BA)

Liquid/vapor equilibrium data on these VOC's in the listed sur-
factants were measured experimentally with varied concentrations
of the VOC's. The surfactants are:

Octylphenyl Decaethoxylate (OPD)

Sorbitan Monooleate (SM)

Sodium Sulfonate (SS)

This limited surfactant set was not used to determine the trends
of surfactant affects on the absorption of the organics. They

serve only as an initial set of surfactants and further studies with additional surfactants are definitely needed.

The results are presented as vapor-liquid equilibrium curves, plotted in several different ways:

i. Each individual VOC at four temperatures between 22 C to 70 C in the respective surfactants Octylphenyl Decaethoxylate, Sorbitan Monooleate and Sodium Sulfonate. Liquid phase concentration ranges vary from 0.05 to 0.45 mole fraction.

ii. Vapor/liquid concentrations for all the five organics in the respective surfactants. At the individual temperatures: 22 C, 40 C, 60 C and 70 C. Liquid phase concentration ranges vary from 0.05 to 0.45 mole fraction.

iii. Vapor/liquid equilibria data for each organic at each of the four respective temperatures in all surfactants(the different absorption capacity of each surfactant).

In Fig. IV-1 to IV-47, we illustrate data for

-- Methyl-ethyl Ketone,

-- Toluene,

-- Acetone,

-- Butyl Acetate

-- i-Propanol

and different surfactants:

Octylphenyl Decaethoxylate,

Sorbitan Monooleate

Sodium Sulfonate

For absorption where there is only sufficiently low concentration of volatile organic chemicals in the surfactant, the equilibrium relationship between fluid and absorbed phase may be linear. This linearity can be expressed by Henry's law, in terms of partial pressure as follow(30):

$P_i = He \ A^*$

here A^* is the concentration of dissolved gas in equilibrium, P_i is the partial pressure of the gas over the liquid and He is the 'Henry's law constant'. For comparing the solubility, we put the Henry's law constants for the five VOC's in three surfactants(Tables IV-1 to IV-6).

The Henry's law constant is also a function of temperature, the relationship is given by:

$d \ln (He) \ / \ d \ (1/T) = \triangle H/R$

where

T is the absolute temperature

R the gas-constant

$\triangle H$ is the heat of absorption (a negative quantity) of the gas into the surfactant in the temperature range studied.

Thus, a plot of log (He) verses 1/T is usually, to a first approximation, a straight line over range of temperature small enough for $\triangle H$ to be effectively constant. This can then be used for predicting solubilities at various temperatures, but we have not done this heat of solution calculation in this thesis.

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A. Effects of Temperature On Vapor-liquid Equilibrium

Experiments were performed to examine the absorption of five solvents with wide range of vapor pressures verses temperature into the three surfactants under the experimental conditions relevant to air stripping technologies. The temperature was varied from room temperature to 70 C. Thus we explored the possible ranges of temperature that would be feasible in an actual scrubbing situation. The specific temperatures were 22 C, 40 C, 60 C and 70 C. We found that temperature has a significant effect on the organic solubility in surfactant.

The vapor phase verses liquid phase mole fractions for each individual VOC at four temperatures between 22 C to 70 C in the respective surfactants: Octylphenyl Decaethoxylate, Sorbitan Monooleate and Sodium Sulfonate for 0.05 to 0.45 liquid mole fractions is presented in Figures IV--1 to IV--15. Table IV--1 to IV--3 also list the organic species mole fraction in the vapor verses mole fraction in the liquid phase.

As was previously noted, the vapor pressure of a gas in a liquid phase equals the partial pressure of the gas in the gaseous phase upon saturation of the liquid. The partial pressure of a gas above a liquid decreases as the liquid absorbs the gas. The vapor pressure in the liquid will increase until equilibrium is achieved in a closes system. The closed system here is our septum capped 40 ml vial and this reduction in partial pressure

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with time represents a reduction in concentration of the organic compound in the vapor phase, This indicates on increase in its vapor pressure in the surfactant and tells us the solubility of organic in the surfactant. The converse is also true, an increase in organic concentration in the vapor state would mean an increase in partial pressure and thus a reduction of the vapor pressure of the organic in the liquid-surfactant system, i.e. a reduction in solubility.

By comparing the mole fraction of the organics in the vapor phase to the mole fraction of the organics in the liquid phase of surfactant, we determined the differences in solubility of the organic compound in the different surfactant solutions over the temperature range of our experiments.

We present figures to illustrate these differences in solubility in several ways. The following discussion will try to describe the patterns and trends of the various target organics effected by the different temperatures, in the respective surfactants.

Octylphenyl Decaethoxylate

Figures IV--1 to IV--5 illustrate the changes of the mole fraction in vapor phase of the five solvents as the temperature increases from 22 to 70 C for absorbent Octylphenyl Decaethoxylate at liquid mole fraction concentrations of 0.05 to 0.45.

The volatile organics
--Toluene

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--Acetone

--i-Propanol

all follow Henry's law for temperatures between 22 and 70 C and liquid concentrations (w/w) below 0.5.

MEK and Butyl Acetate follow Henry's law only at the higher temperatures (above 60 C). For these two VOC's the data indicate a definite trend toward finite vapor pressure at 0.0 liquid mole fraction

Sorbitan Monooleate

Figure IV--6 to IV--10 indicate for:

-- Toluene

-- i-Propanol

-- Acetone

All these volatile organics follow Henry's law for temperatures between 22 to 70 C and liquid concentrations (w/w) below 0.4 liquid phase mole fraction.

MEK follows Henry's law only at the 70 C, Butyl Acetate not obey Henry's law in this absorbent over the temperature range of 22 to 70 C. For MEK the data indicate a definite trend toward finite vapor pressure at 0.0 liquid mole fraction.

Sodium Sulfonate

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Figures IV-11 to IV-15 show that for sorbent Sodium Sulfonate, volatile organics

-- Toluene

-- Acetone

-- i-Propanol

all follows Henry's law for temperatures between 22 and 70 C and liquid concentrations (w/w) below 0.4.

Butyl Acetate follow Henry's law only at the higher temperature (above 40 C), and MEK does not obey Henry's law in this sorbent over the temperature range of 22 to 70 C. For these two VOC's the data indicate a definite trend toward finite vapor pressure at 0.0 liquid mole fraction.

Data in Tables IV 8--10 illustrate on the effects of temperature by presenting the y:x ratio, where y is mole fraction of organics in vapor phase, and x is mole fraction of organics in liquid phase. Table IV-11 to 14 list these vapor/liquid ratios for five organic solvents in the three surfactants at four temperatures. For example, the vapor/liquid ratio of MEK increases by 2.4, 2.7, 2.9 times in the respective surfactants OPD, SM and SS when the temperature rises from 23 C to 70 C.

There is a direct proportional relationship between the organic solvents mole fraction in vapor phase and the temperature. For all the VOC-surfactant systems, the organic vapor pressure increases as the temperature increases. We can make the general statement that the VOC's vapor concentration in VOC-

surfactant systems are directly effected by the temperature. This fact is presented in Tables IV-1 to IV-6 which list Henry's law constants for the five VOC's in three surfactants.

B. Relative Solubilities Of The Target Volatile Organic Compounds (VOC's) In Surfactants

The five organic solvents have different solubility in three surfactants over the temperature range of these experiments. Figures IV-16 to IV-27 show the relative trends in solubility of the target volatile organic compounds.

Fig. IV--16 to IV--19, illustrate that the mole fraction of Acetone in vapor phase is the highest of all organic solvents in Octylphenyl Decaethoxylate.

MEK and i-Propanol have relatively moderate solubilities in Octylphenyl Decaethoxylate (see Fig. IV--16, 17, 18 and 19.) in the temperature range 40 to 70 C. The lower mole fractions of MEK and i-Propanol in vapor phase than Acetone at same conditions indicates that they have higher solubility.

i-Propanol shows some what higher solubility and lower vapor pressures at 22 C than MEK. At 40 - 70 C, however, the two organics show similar solubilities with a small trend to a larger Henry's law constant (steeper slope) for i-Propanol. Relative to MEK, at the 40 - 70 C range i-Propanol has a slightly lower

solubility at the Higher liquid mole fractions. I-Propanol follows Henry's law more closely over all temperature than MEK.

The trend in solubility of Butyl Acetate is similar to Toluene, both have high solubilities in Octylphenyl Decaethoxylate at all temperatures. There appears to be a slightly higher solubility for Butyl Acetate at the higher temperature and in higher liquid concentrations. The lower mole fractions of Butyl Acetate and Toluene in vapor phase relative to the other three organic solvents under same conditions show that these two VOC's can be more easily scrubbed from the air by the surfactants.

Fig. IV--20 to IV--23 show the following relative trends in solubility for Sorbitan Monooleate.

-- Acetone

Experimental data at all temperatures indicate that the mole fraction of Acetone in vapor phase is the highest of all organic solvents in Sorbitan Monooleate. For example, the mole fraction in vapor 1.7E-01 at 70 C when mole fraction in liquid is 0.4; this is 15 fold of that of Toluene (1.20E-02) under the same conditions. Acetone appears to follow Henry's law for all temperatures and shows the lowest solubility of all the organics in these experiments.

MEK and i-Propanol have relatively moderate solubilities in Sorbitan Monooleate (Fig. IV--20, 21, 22 and 23). The lower mole

fractions of MEK and i-Propanol in vapor phase than Acetone under the same conditions shows that they are more soluble in this surfactant than Acetone. Temperature is observed to have more effect on isopropanol than on MEK. At 22 C, i-Propanol shows significantly higher solubility and lower vapor pressures than MEK. When the temperature is above 40 C (40 to 70 C), the two curves have shown similar solubilities of two organics with a trend to similar Henry's law constants. Relative to i-Propanol, MEK has a slightly lower solubility at the higher liquid mole fractions for the 40 to 70 C range. i-Propanol follows Henry's law only at 70 C in this sorbent.

Butyl Acetate and Toluene also exhibit similar results in Sorbitan Monooleate (see Fig. IV--20, 21, 22 and 23.). The lower mole fractions of Butyl Acetate and Toluene in vapor phase than the other three organic solvents at same conditions show that they are more soluble. Both have relatively high solubilities in Sorbitan Monooleate at all temperatures. There appears to be a slightly higher solubility for Toluene in the temperature range 40 to 70 C and at higher liquid concentrations than Butyl Acetate in this sorbent. This is different from the their relative trends in solubility in Octylphenyl Decaethoxylate under the same conditions.

Figures IV-24 to IV-27 present the following relative trends in solubility for Sodium Sulfonate.

Acetone again exhibits the highest vapor pressure of all the VOC's in this Sodium Sulfonate surfactant(Fig. IV--24 to 27). The mole fraction in vapor phase increase from 1.4E-01 to 3.8E-02 when the mole fraction of Acetone in liquid phase increases from 0.055 to 0.385 at 70 C. This organic solvent appears to follow Henry's law for all temperature and shows the lowest solubility of all the solvents in this experiment.

MEK and i-Propanol have similar moderate solubilities in Sodium Sulfonate (Fig. IV--24 to 27). The lower mole fractions of MEK and i-Propanol in vapor phase than Acetone at same conditions shows a higher solubility over that of Acetone. At 22 and 40 C, i-Propanol shows significantly higher solubility and lower vapor pressures than MEK. When the temperature rises to 60 - 70 C, the two organics show similar solubilities with a small trend to a larger Henry's law constant (steeper slope) for i-Propanol relative to MEK. For the 60 to 70 C range, i-Propanol has a slightly lower solubility at the higher liquid mole fractions. i-Propanol follows Henry's law more closely over all temperature than MEK in this Sodium Sulfonate surfactant.

Butyl Acetate and Toluene exhibit very similar vapor mole fraction curves in Sorbitan Monooleate (Fig. IV--20 to 23). The lower mole fractions of Butyl Acetate and Toluene in vapor phase than the other three organic solvents again shows that they are more soluble in this surfactant.

There are certain similarities between the VOC's behavior in

all of the surfactants. Close examination shows that except for one or two points, the trends and related positions of Acetone, Toluene and Butyl Acetate curves are also quite similar for the same organic concentrations (w/w) in each surfactant. The mole fractions in vapor state decrease in the following order: Acetone, MEK, i-Propanol, Butyl Acetate, Toluene; the solubilities in liquid state increase in the reverse order. Toluene is absorbed more readily in all three surfactants. The above characteristics can also be observed distinctly in Tables IV--4 to 7.

One important factor which effects the solubility of organic compounds significantly is their boiling point. This point can be observed readily by comparing the order of organic mole fraction in vapor from high to low to the order of their boiling points(see Table II-2).

C. Comparison Of Surfactants Absorption

The effect of surfactant on the solubilities of the five organic compounds can be seen in Figures IV--28 to IV--47. Tables IV--4 to IV--8 also express the vapor liquid mole fraction ratios of organic compounds with temperature and liquid phase mole fraction.

Figure IV--28 to IV--31 show the MEK vapor/liquid equilibria data for each organic at the four respective temperatures in all surfactants: Octylphenyl Decaethoxylate, Sorbitan Monooleate and Sodium Sulfonate at 23, 40, 60, and 70 C.

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MEK has the lowest relative solubility in Sodium Sulfonate where it also most closely follows Henry's law. MEK has the highest solubility in Octylphenyl Decaethoxylate where it has the highest deviation from Henry's law (shown as an extrapolated positive vapor pressure at 0.0 liquid concentration). At 23 C, the vapor concentration of MEK is 2.5E-02 in Sodium Sulfonate which is 1.5 times of that in Octylphenyl Decaethoxylate, when the liquid phase organic concentration is 8% (w/w) in the surfactant.

Sorbitan Monooleate surfactant is intermediate in solubility for MEK over the all temperatures and liquid concentration ranges.

Higher temperatures show a trend toward improved Henry's law behavior.

Octylphenyl Decaethoxylate and Sodium Sulfonate still show significant deviations at 40 C.

Toluene

The effect of the three individual surfactants on solubility of Toluene at all temperatures is shown at Figure IV--32 to IV--35 respectively. The solubility of Toluene is the lowest in Sodium Sulfonate where it also most closely follows Henry's law. Toluene has the highest solubility in Octylphenyl Decaethoxylate where it has the highest deviation from Henry's law

shown as an extrapolated positive vapor pressure of 2.2E-02 mole fraction. For example, at 23 C, the vapor concentration of Toluene is 1.0E-03 in Sodium Sulfonate which is 2.2 times of that in Octylphenyl Decaethoxylate (5.2E-04) when the liquid phase organic concentration is 8% (w/w).

Sorbitan Monooleate surfactant is intermediate in solubility for Toluene over the all the temperature and liquid ranges.

Toluene appears to follow Henry's law best in Octylphenyl Decaethoxylate.

Butyl Acetate

The solubility of Butyl Acetate is presented for comparison with three surfactants Octylphenyl Decaethoxylate, Sorbitan Monooleate and Sodium Sulfonate at 22, 40, 60 and 70 C respectively in Figures IV--36 to IV--39. At all temperatures, Butyl Acetate has lowest relative solubility in Sorbitan Monooleate where it also most closely follows Henry's law. Butyl Acetate has the highest solubility in Sodium Sulfonate at 22 C and in Octylphenyl Decaethoxylate at 40, 60 and 70 C where it also has relative higher deviation from Henry's law. For example, at 23 C, the vapor concentration of Butyl Acetate is 0.5E-02 in Sorbitan Monooleate which is 2.3 times of that in Sodium Sulfonate, when the organic concentration is 8% (w/w) in surfactant liquid.

Higher temperatures show a trend toward improved Henry's law behavior for Butyl Acetate.

Acetone

Figure IV--40 to IV--43 show the effect of the three surfact-
ants on the solubilities of Acetone at four temperatures respec-
tively. At 60 C and 70 C,   Acetone has the lowest relative
solubility in Sorbitan Monooleate where it also follows Henry's
law. Acetone has the lowest relative solubility in Sodium Sulfo-
nate at 22 and 40 C. It has the highest solubility in Octylphenyl
Decaethoxylate where it follows Henry's law. For example, at 23
C, the vapor concentration of Acetone is 8.3E-02 in Sodium
Sulfonate which is 1.5 times of that in Octylphenyl Decaethoxy-
late(5.4E-02) when organic concentration is 8% (w/w) in surfact-
ant.

Acetone appears to follow Henry's law in all three surfactants
over the all temperature ranges.

I-Propanol

Figure IV--44 to IV--47 indicate the solubilities of i-Propa-
nol in the three surfactants at 22, 40, 60 and 70 C respective-
ly. The lowest relative solubility of this organic compound is
shown in Sodium Sulfonate where it is shown to follow Henry's
law. i-Propanol has the highest solubility in Octylphenyl Dec-
aethoxylate where it also follows Henry's law. For example, at
23 C, the vapor concentration of i-Propanol is 1.5E-02 in Sodium
Sulfonate which is 0.9 times of that in Octylphenyl Decaethoxy-
late, when organic concentration is 8% (w/w) in surfactant.

60

Sorbitan Monooleate surfactant is intermediate in solubility for i-Propanol over the all temperature and liquid concentration ranges.

Higher temperatures show a trend toward improved Henry's law behavior. Octylphenyl Decaethoxylate and Sorbitan Monooleate show significant deviations, however, at 22 C.

i-Propanol appears to follow Henry's law in all three surfactants over the all temperature and liquid concentration ranges.

Tables IV--4 to IV--7, show that each organic compound appears to have lowest vapor/liquid mole fraction ratio in Octylphenyl Decaethoxylate among the three surfactants all temperatures. This indicates Octylphenyl Decaethoxylate is most efficient (has highest solubility) for these organic compounds among the three surfactants we studied.

Table IV-1. Henry's Law Constants for Acetone, Butyl Acetate and Toluene in Octylphenyl Decaethoxylate

Temp. (C)	Conc. %(v/v)	He* (Atm) (Liter) / mole		
		Acetone	Butyl Acetate	Toluene
23	1	6.1E-02	1.3E-02	3.3E-03
	2	5.9E-02	9.8E-03	3.7E-03
	4	5.3E-02	6.9E-03	4.5E-03
	8	4.4E-02	5.0E-03	3.5E-03
40	1	9.8E-02	1.4E-02	1.0E-02
	2	8.3E-02	1.1E-02	9.1-E03
	4	8.1E-02	7.0E-03	7.9E-03
	8	8.4E-02	5.7E-03	6.1E-03
60	1	1.3E-01	2.0E-02	1.8E-02
	2	1.3E-01	1.5E-02	1.7E-02
	4	1.1E-01	1.2E-02	1.5E-02
	8	8.3E-02	1.3E-02	1.3E-02
70	1	1.6E-01	2.5E-02	2.3E-02
	2	1.4E-01	1.9E-02	2.1E-02
	4	1.4E-01	1.7E-02	2.1E-02
	8	1.1E-01	1.5E-02	2.1E-02

* He: Henry's Law Constant

Table IV-2. Henry's Law Constants for Methyl-ethyl Ketone and i-Propanol in Octylphenyl Decaethoxylate

Temp. (C)	Conc. %(v/v)	He* (Atm) (Liter) / mole Methyl-ethyl Ketone	i-Propanol
23	1	5.0E-02	1.1E-02
	2	3.4E-02	1.4E-02
	4	2.5E-02	1.3E-02
	8	1.7E-02	1.1E-02
40	1	5.2E-02	3.4E-02
	2	4.0E-02	3.2E-02
	4	3.0E-02	2.8E-02
	8	2.1E-02	2.4E-02
60	1	6.3E-02	5.1E-02
	2	4.3E-02	4.5E-02
	4	4.7E-02	4.1E-02
	8	3.6E-02	4.0E-02
70	1	8.0E-02	9.3E-02
	2	6.1E-02	6.8E-02
	4	5.6E-02	8.1E-02
	8	4.2E-02	7.0E-02

* He: Henry's Law Constant

Table I-3. Henry's Law Constants for Acetone, Butyl Acetate and Toluene in Sorbitan Monooleate

Temp. (C)	Conc. %(v/v)	He* (Atm) (Liter) / mole Acetone	Butyl Acetate	Toluene
25	1	7.2E-02	5.5E-02	6.8E-03
	2	5.4E-02	3.0E-02	6.3E-03
	4	5.8E-02	1.3E-02	5.3E-03
	8	4.1E-02	8.2E-03	4.6E-03
40	1	9.9E-02	6.3E-02	1.9E-02
	2	7.4E-02	3.3E-02	1.6E-02
	4	7.1E-02	1.7E-02	1.2E-02
	8	7.1E-02	1.1E-02	9.0E-03
60	1	1.8E-01	6.7E-02	2.0E-02
	2	1.4E-01	3.9E-02	2.1E-02
	4	1.2E-01	2.4E-02	1.4E-02
	8	1.2E-01	1.7E-02	1.1E-02
70	1	1.8E-01	6.8E-02	2.7E-02
	2	1.5E-01	4.1E-02	2.4E-02
	4	1.3E-01	2.9E-02	2.2E-02
	8	1.5E-01	2.2E-02	1.4E-02

* He: Henry's Law Constant

Table IV-4 Henry's Law Constants for Methyl-ethyl Ketone and i-Propanol in Sorbitan Monooleate

Temp.	Conc.	He* (Atm) (Liter) / mole	
(C)	%(v/v)	Methyl-ethyl Ketone	i-Propanol
24	1	5.2E-02	3.6E-02
	2	3.6E-02	2.9E-02
	4	2.7E-02	2.0E-02
	8	2.0E-02	1.3E-02
40	1	5.2E-02	5.0E-02
	2	4.5E-02	3.2E-02
	4	3.1E-02	2.8E-02
	8	2.4E-02	1.8E-02
60	1	7.7E-02	6.1E-02
	2	6.5E-02	5.2E-02
	4	4.3E-02	5.0E-02
	8	3.6E-02	2.9E-02
70	1	8.8E-02	8.2E-02
	2	8.6E-02	9.6E-02
	4	5.8E-02	8.0E-02
	8	6.3E-02	8.2E-02

* He: Henry's Law Constant

Table IV-5 Henry's Law Constants for Methyl-ethyl Ketone and i-Propanol in Sodium Sulfonate

Temp. (C)	Conc. %(v/v)	He* (Atm) (Liter) / mole Methyl-ethyl Ketone	i-Propanol
21	1	9.5E-02	3.7E-02
	2	5.6E-02	2.6E-02
	4	3.4E-02	2.2E-02
	8	2.7E-02	1.4E-02
40	1	1.1E-01	3.9E-02
	2	6.5E-02	3.2E-02
	4	4.4E-02	3.3E-02
	8	3.7E-02	2.5E-02
60	1	1.3E-01	7.5E-02
	2	9.0E-02	6.3E-02
	4	6.4E-02	5.7E-02
	8	6.3E-02	5.2E-02
70	1	1.8E-01	1.4E-01
	2	1.2E-01	1.1E-01
	4	9.7E-02	1.1E-01
	8	8.6E-02	9.2E-02

* He: Henry's Law Constant

Table IV-6 Henry's Law Constants for Acetone, Butyl Acetate and Toluene in Sodium Sulfonate

Temp. (C)	Conc. %(v/v)	He* (Atm) (Liter) / mole		
		Acetone	Butyl Acetate	Toluene
22	1	7.5E-02	1.1E-02	1.3E-02
	2	7.2E-02	7.9E-03	1.2E-02
	4	8.0E-02	5.3E-03	1.1E-02
	8	6.5E-02	3.9E-03	7.1E-03
40	1	1.2E-01	1.4E-02	2.6E-02
	2	9.5E-02	9.3E-03	2.1E-02
	4	8.5E-02	9.0E-03	1.6E-02
	8	6.3E-02	8.1E-03	1.6E-02
60	1	2.0E-01	2.2E-02	3.1E-02
	2	1.2E-01	2.1E-02	2.9E-02
	4	1.0E-01	1.4E-02	2.1E-02
	8	1.1E-01	1.5E-02	2.3E-02
70	1	3.2E-01	2.9E-02	3.8E-02
	2	2.1E-01	2.8E-02	3.8E-02
	4	1.4E-01	1.9E-02	2.9E-02
	8	1.1E-01	2.0E-02	3.2E-02

* He: Henry's Law Constant

Table IV-7.   Henry's Law Constants (average values)

Solvent	Temp. (C)	Surfactant OPD	SM	SS
Acetone	23	4.9E-02	5.0E-02	7.3E-02
	40	8.7E-02	7.2E-02	7.4E-02
	60	1.1E-01	1.4E-01	1.1E-01
	70	1.4E-01	1.5E-01	1.3E-01
Butyl Acetate	23	6.0E-03	1.1E-02	9.2E-03
	40	6.4E-03	1.4E-02	8.7E-03
	60	1.5E-02	2.1E-02	1.5E-02
	70	1.6E-02	2.6E-02	2.0E-02
Toluene	23	3.8E-03	5.0E-03	1.2E-02
	40	7.0E-03	1.1E-02	1.6E-02
	60	1.4E-02	1.3E-02	2.2E-02
	70	2.2E-02	2.0E-02	3.4E-02
MEK	23	2.1E-02	2.4E-02	3.1E-02
	40	2.6E-02	2.8E-02	4.1E-02
	60	4.2E-02	4.0E-02	6.4E-02
	70	4.9E-02	6.1E-02	9.2E-02
i-Propanol	23	1.2E-02	1.7E-02	1.8E-02
	40	2.6E-02	2.3E-02	2.9E-02
	60	4.4E-02	4.0E-02	5.5E-02
	70	7.8E-02	8.5E-02	1.1E-01

Table IV--8. Y:X Ratio of Organic Mole Fraction in

Octylphenyl Decaethoxylate

Solvent	Room Temp.	40 C	60 C	70 C
MEK	6.4E-02	7.5E-02	1.1E-01	1.6E-01
Toluene	7.7E-03	1.5E-02	3.0E-02	4.4E-02
Butyl Acetate	1.2E-02	1.3E-02	2.3E-02	3.2E-02
Acetone	1.1E-01	1.7E-01	2.4E-01	2.8E-01
i-Propanol	2.6E-02	6.0E-02	8.90E-02	1.8E-01

Y: mole fraction of organics in vapor phase;

X: mole fraction of organics in surfactant.

Table IV--9. Y:X Ratio of Organic Solvent in Sorbitan Monooleate

Solvent	Room Temp.	40 C	60 C	70 C
MEK	7.3E-02	8.7E-02	1.3E-01	2.0E-01
Toluene	1.4E-02	2.9E-02	3.4E-02	4.5E-02
Butyl Acetate	2.5E-02	3.2E-02	4.9E-02	6.2E-02
Acetone	1.5E-01	2.2E-01	3.8E-01	4.6E-01
i-Propanol	4.9E-02	6.6E-02	1.1E-01	1.9E-01

Y: mole fraction of organics in vapor phase;

X: mole fraction of organics in surfactant.

Table IV--10. Y:X Ratio of Organic Solvent in Sodium Sulfonate

Solvent	Room Temp.	40 C	60 C	70 C
MEK	8.8E-02	1.2E-01	1.9E-01	2.6E-01
Toluene	2.1E-02	4.5E-02	6.5E-02	8.8E-02
Butyl Acetate	1.1E-02	2.1E-02	3.9E-02	5.3E-02
Acetone	2.1E-01	2.2E-01	3.1E-01	4.1E-01
i-Propanol	5.0E-02	7.9E-02	1.5E-01	3.0E-01

Y: mole fraction of organics in vapor phase;

X: mole fraction of organics in surfactant.

Table IV--11. Y:X Ratio of Organic Solvents in Three Surfactants at 22 C

Solvent	Surfactant		
	Octylphenyl Decaethoxylate	Sorbitan Monooleate	Sodium Sulfonate
MEK	6.4E-02	7.3E-02	8.8E-02
Toluene	7.7E-03	1.4E-02	2.1E-02
Butyl Acetate	1.2E-02	2.5E-02	1.1E-02
Acetone	1.1E-01	1.5E-01	2.1E-01
i-Propanol	2.6E-02	4.9E-02	5.0E-02

Y: mole fraction of organics in vapor phase;

X: mole fraction of organics in surfactant.

Table IV--12. Y:X Ratio of Organic Solvents in Three Surfactants at 40 C

Solvent	Surfactant		
	Octylphenyl Decaethoxylate	Sorbitan Monooleate	Sodium Sulfonate
MEK	7.5E-02	8.7E-02	1.2E-01
Toluene	1.5E-02	2.9E-02	4.5E-02
Butyl Acetate	1.3E-02	3.2E-02	2.1E-02
Acetone	1.7E-01	2.2E-01	2.2E-01
i-Propanol	6.0E-02	6.6E-02	7.9E-02

Y: mole fraction of organics in vapor phase;

X: mole fraction of organics in surfactant.

Table IV--13. Y:X Ratio of Organic Solvents in Three Surfactants

at 60 C

Solvent	Surfactant		
	Octylphenyl Decaethoxylate	Sorbitan Monooleate	Sodium Sulfonate
MEK	1.1E-01	1.3E-01	1.9E-01
Toluene	3.0E-02	3.4E-02	6.5E-02
Butyl Acetate	2.3E-02	4.9E-02	3.9E-02
Acetone	2.4E-01	3.8E-01	3.1E-01
i-Propanol	8.90E-02	1.1E-01	1.5E-01

Y: mole fraction of organics in vapor phase;

X: mole fraction of organics in surfactant.

Table IV--14. Y:X Ratio of Organic Solvents in Three Surfactants at 70 C

Solvent	Surfactant		
	Octylphenyl Decaethoxylate	Sorbitan Monooleate	Sodium Sulfonate
MEK	1.6E-01	2.0E-01	2.6E-01
Toluene	4.4E-02	4.5E-02	8.8E-02
Butyl Acetate	3.2E-02	6.2E-02	5.4E-02
Acetone	2.8E-01	4.6E-01	4.1E-01
i-Propanol	1.8E-01	1.9E-01	3.0E-01

Y: mole fraction of organics in vapor phase;

X: mole fraction of organics in surfactant.

Fig. IV--1. MEK MOLE FRACTION
Surfactant:Octylphenyldeca-ethoxyl-OH

Mole Fraction - Vapor Phase(E-02)

Mole Fraction - Liquid Phase

· 23 C   + 40 C   * 60 C   □ 70 C
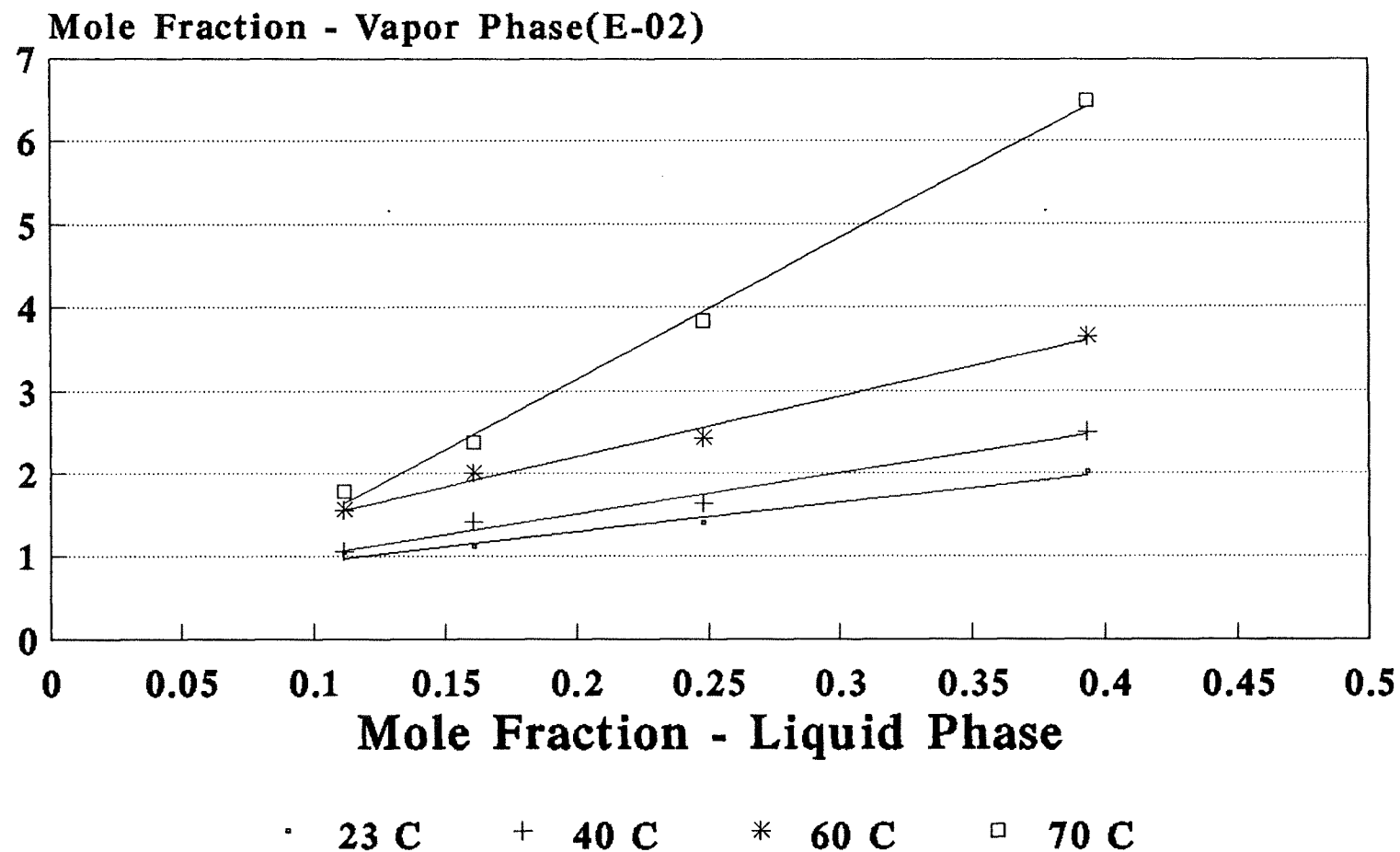
Fig. IV--2 TOLUENE MOLE FRACTION
Surfactant: Octylphenyldeca-ethoxyl-OH

Fig. IV--3 BUTYL ACETATE MOLE FRACTION
Surfactant: Octylphenyldeca-ethoxyl-OH
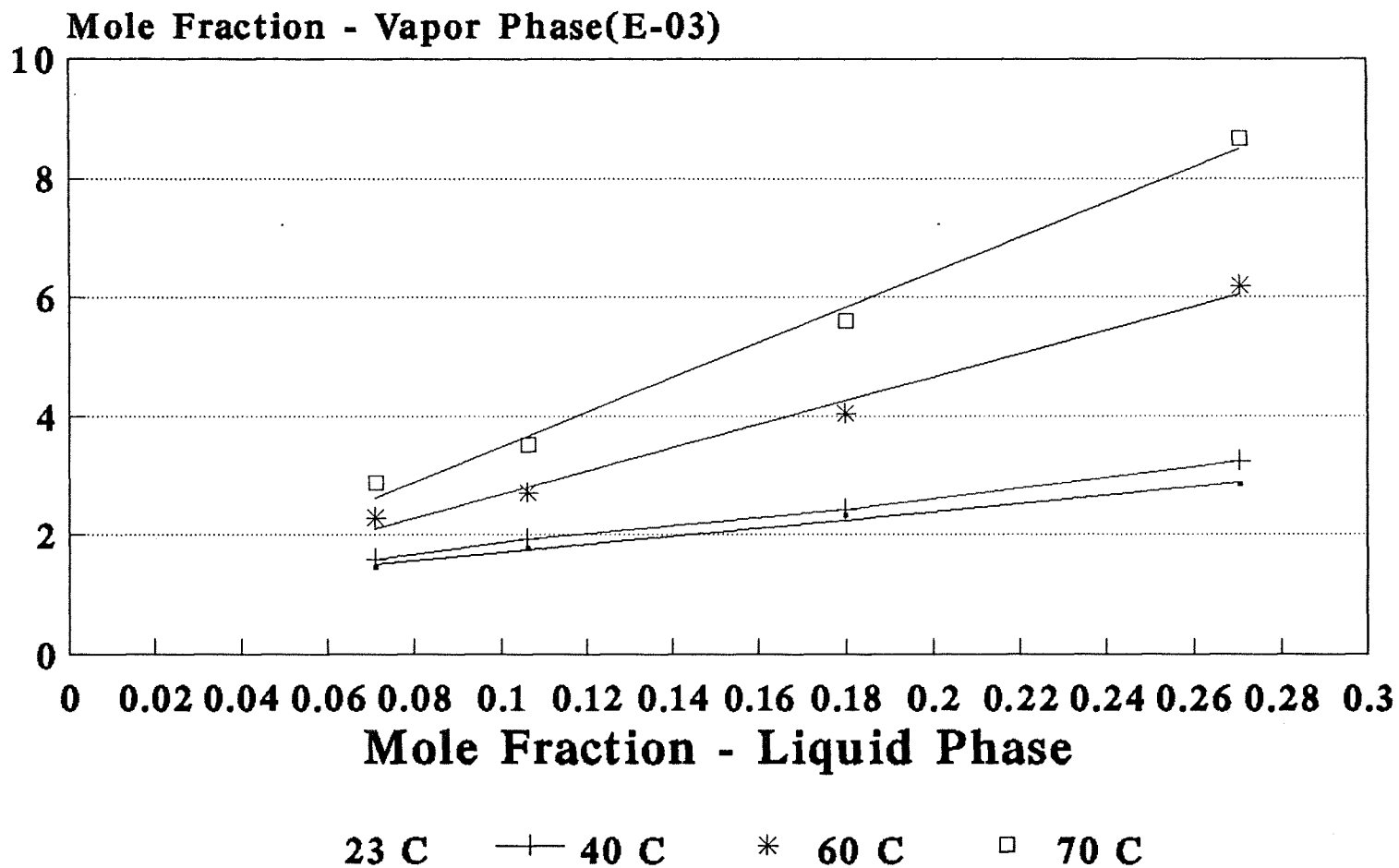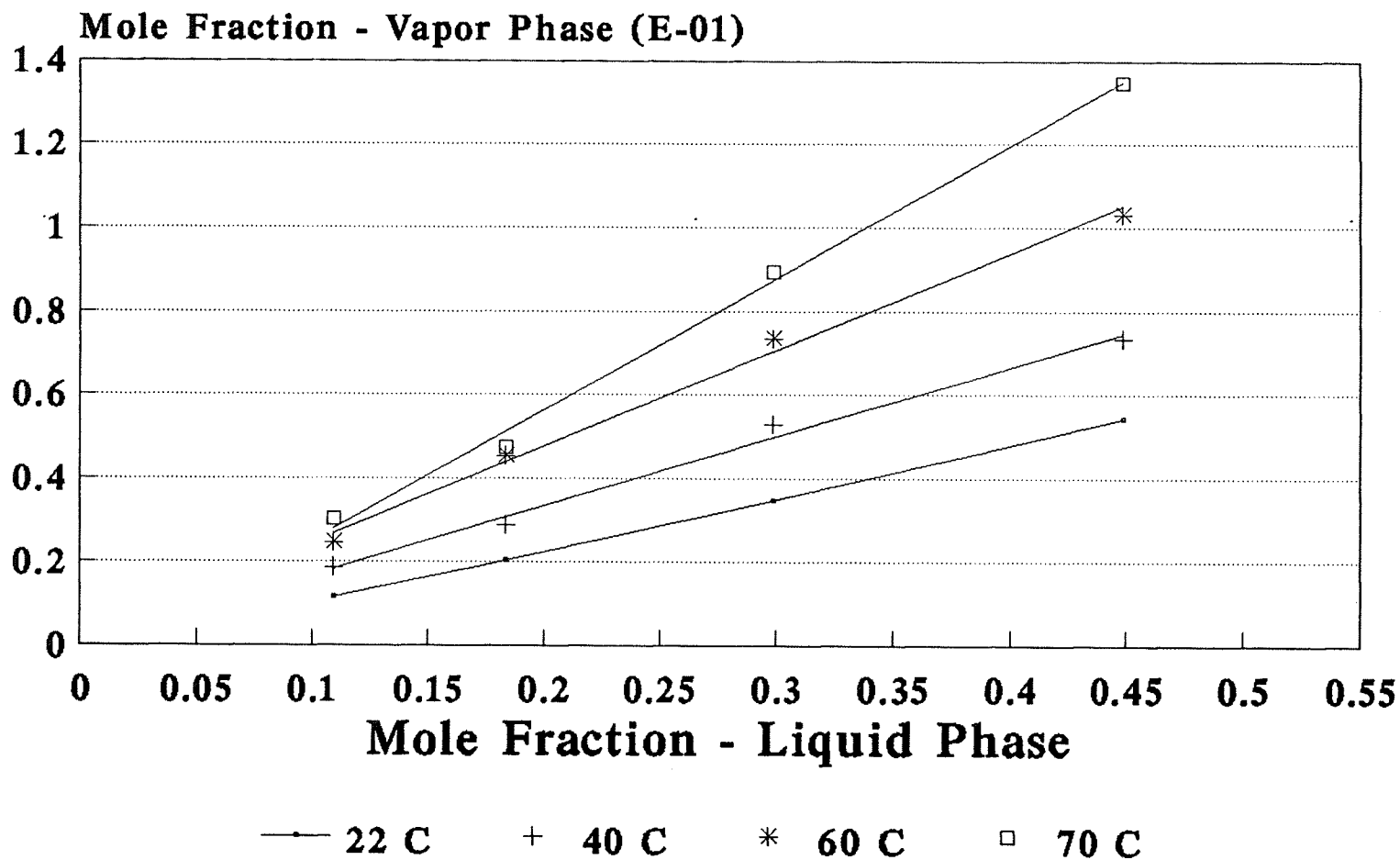
Mole Fraction - Vapor Phase(E-03) vs. Mole Fraction - Liquid Phase

Legend: 23 C   —+— 40 C   * 60 C   □ 70 C

Fig. IV--4 ACETONE MOLE FRACTION
Surfactant: Octylphenyldeca-ethoxyl-OH

Mole Fraction - Vapor Phase (E-01)

Mole Fraction - Liquid Phase

—— 22 C   +   40 C   *   60 C   □   70 C

Fig. IV--5 i-PROPANOL MOLE FRACTION
Surfactant: Octylphenyldeca-ethoxyl-OH

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

— 24 C   —+— 40 C   * 60 C   □ 70 C
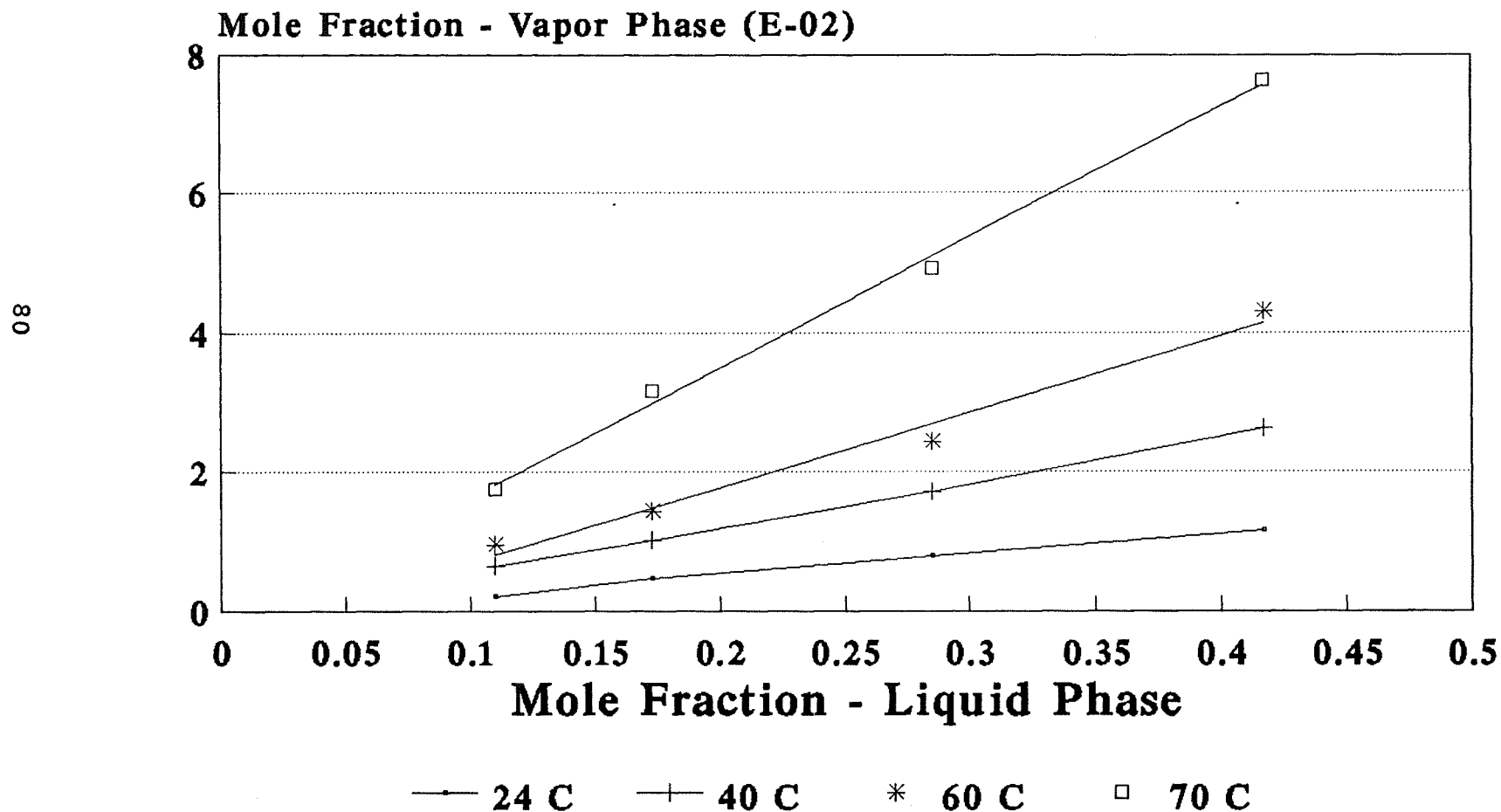
Fig. IV--6. MEK MOLE FRACTION
Surfactant: Sorbitan Monooleate

Mole Fraction - Vapor Phase(E-02)

Mole Fraction - Liquid Phase

—— 23 C   + 40 C   * 60 C   □ 70 C
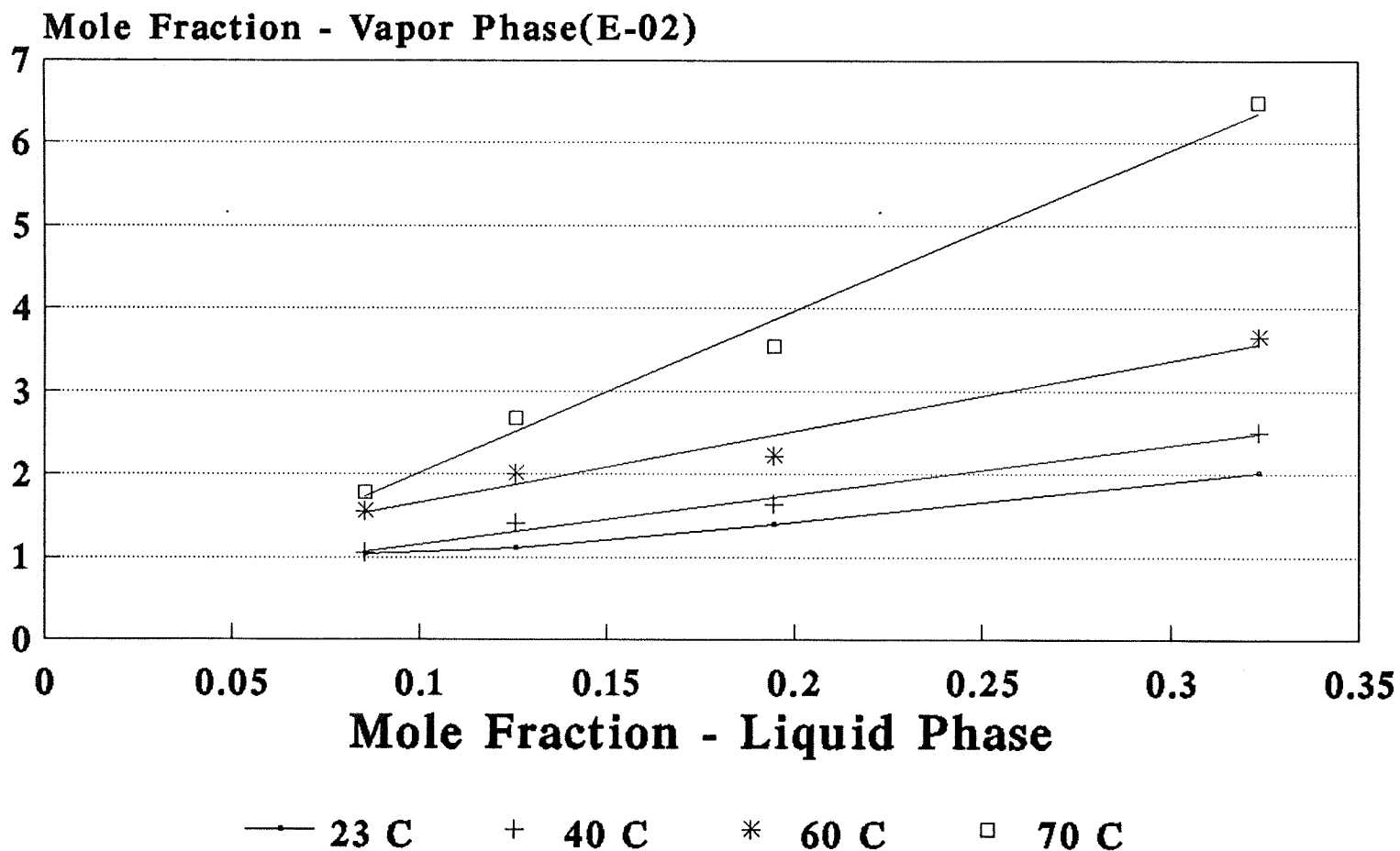
Fig. IV--7 TOLUENE MOLE FRACTION
Surfactant: Sorbitan Monooleate
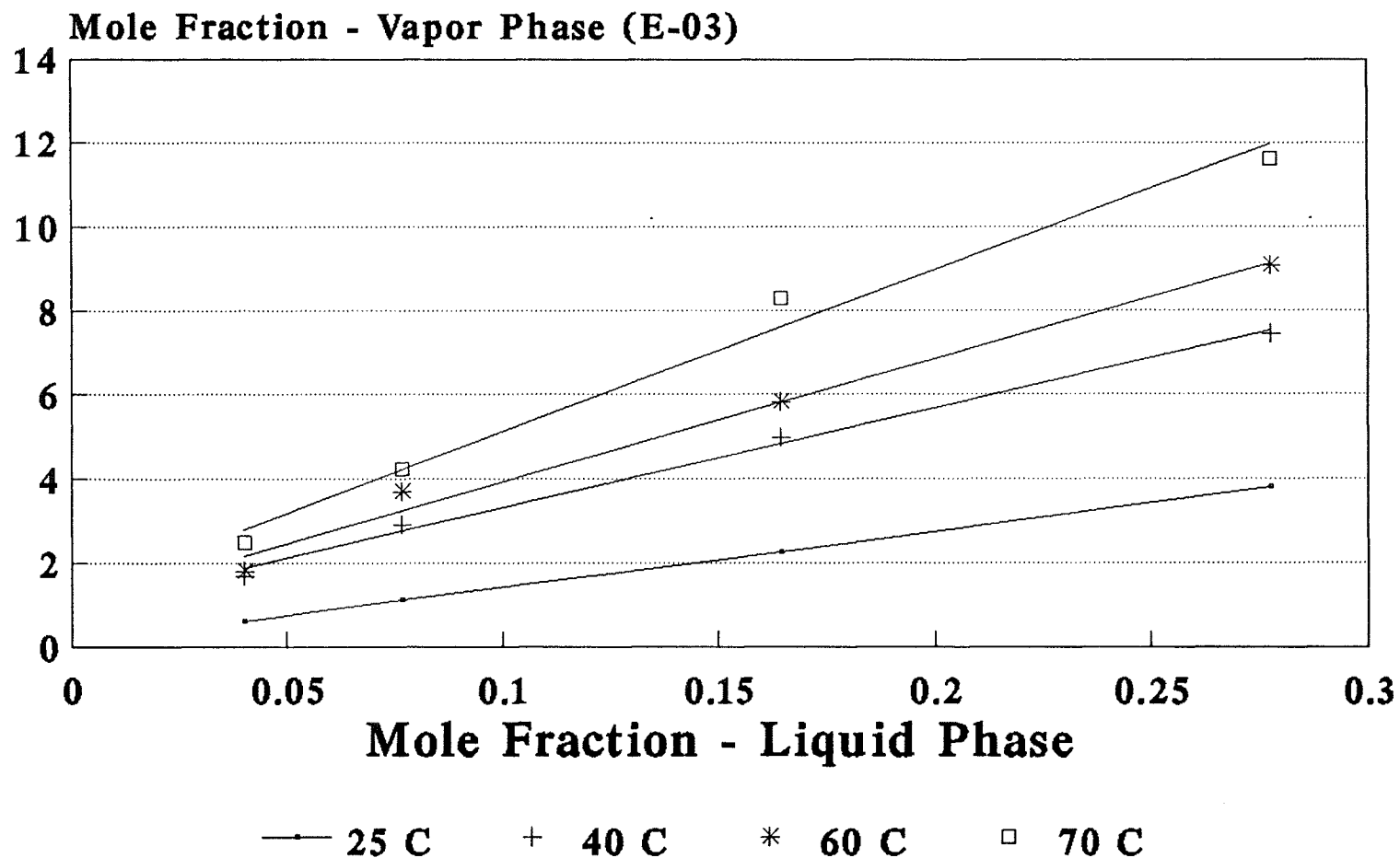
Fig. IV--8 BUTYL ACETATE MOLE FRACTION
Surfactant: Sorbitan Monooleate
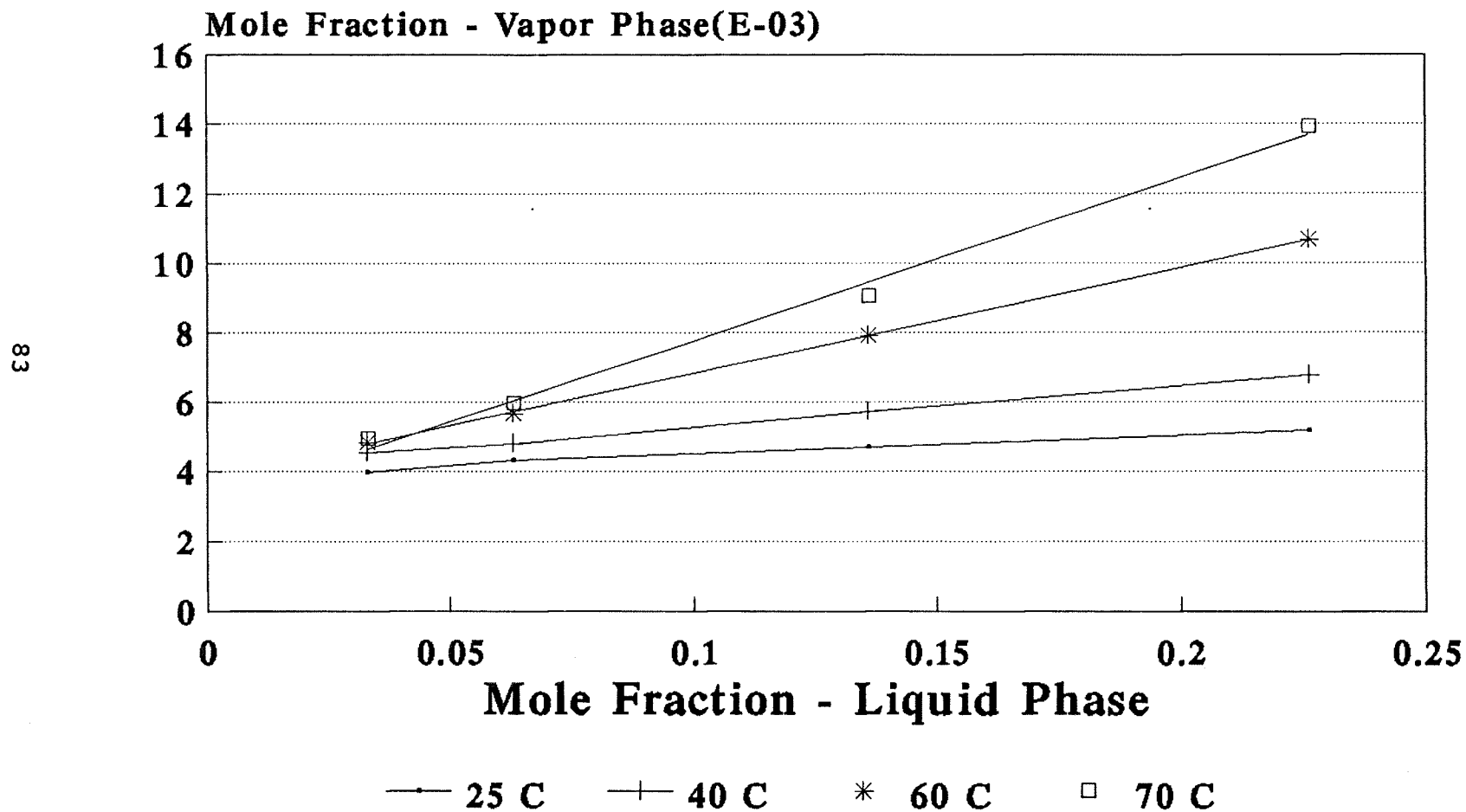
Fig. IV--9 ACETONE MOLE FRACTION
Surfactant: Sorbitan Monooleate
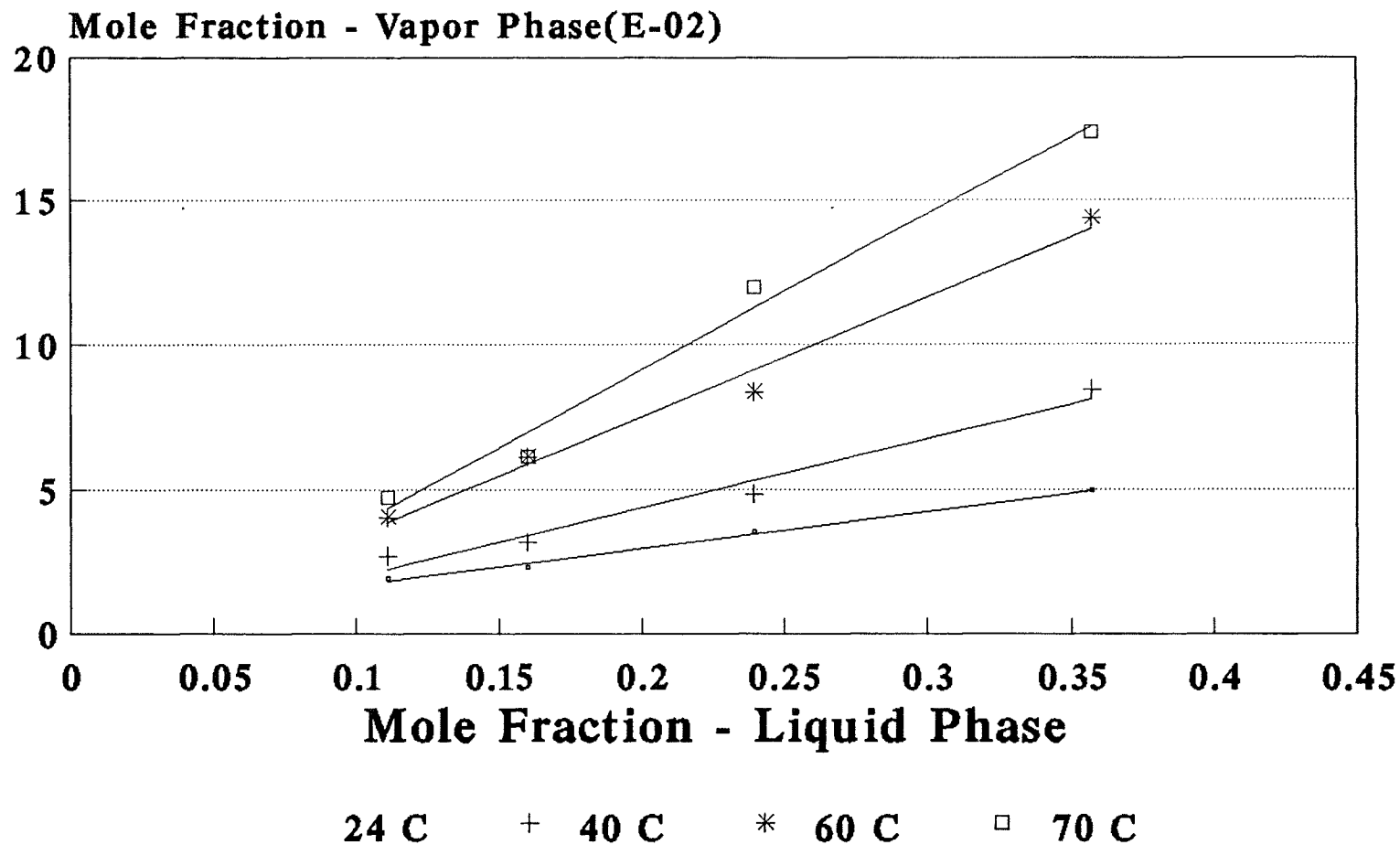
Fig. IV--10 i-PROPANOL MOLE FRACTION
Surfactant: Sorbitan Monooleate

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· 24 C   + 40 C   * 60 C   □ 70 C
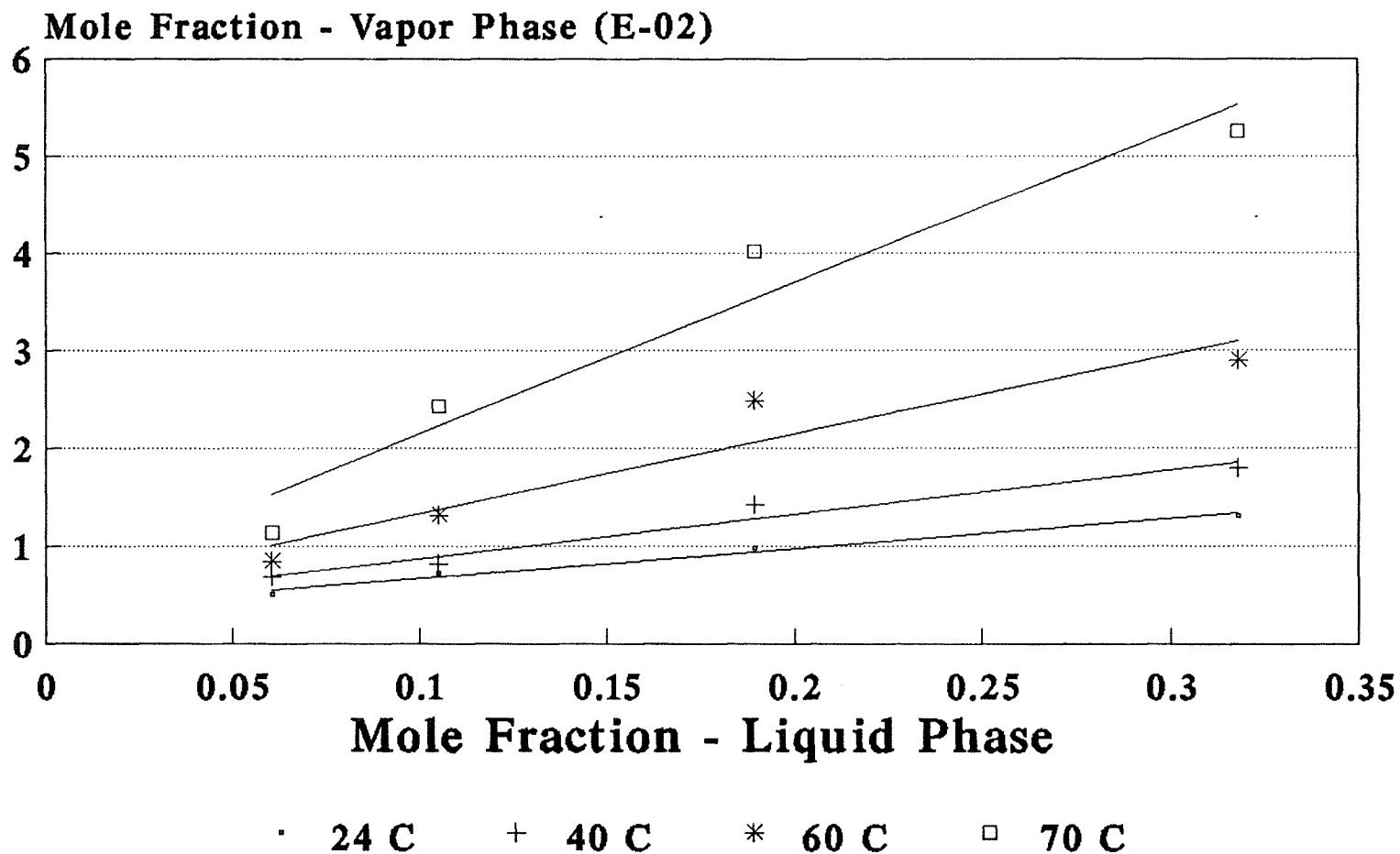
Fig. IV--11 MEK MOLE FRACTION
Surfactant: Sodium Sulfonate
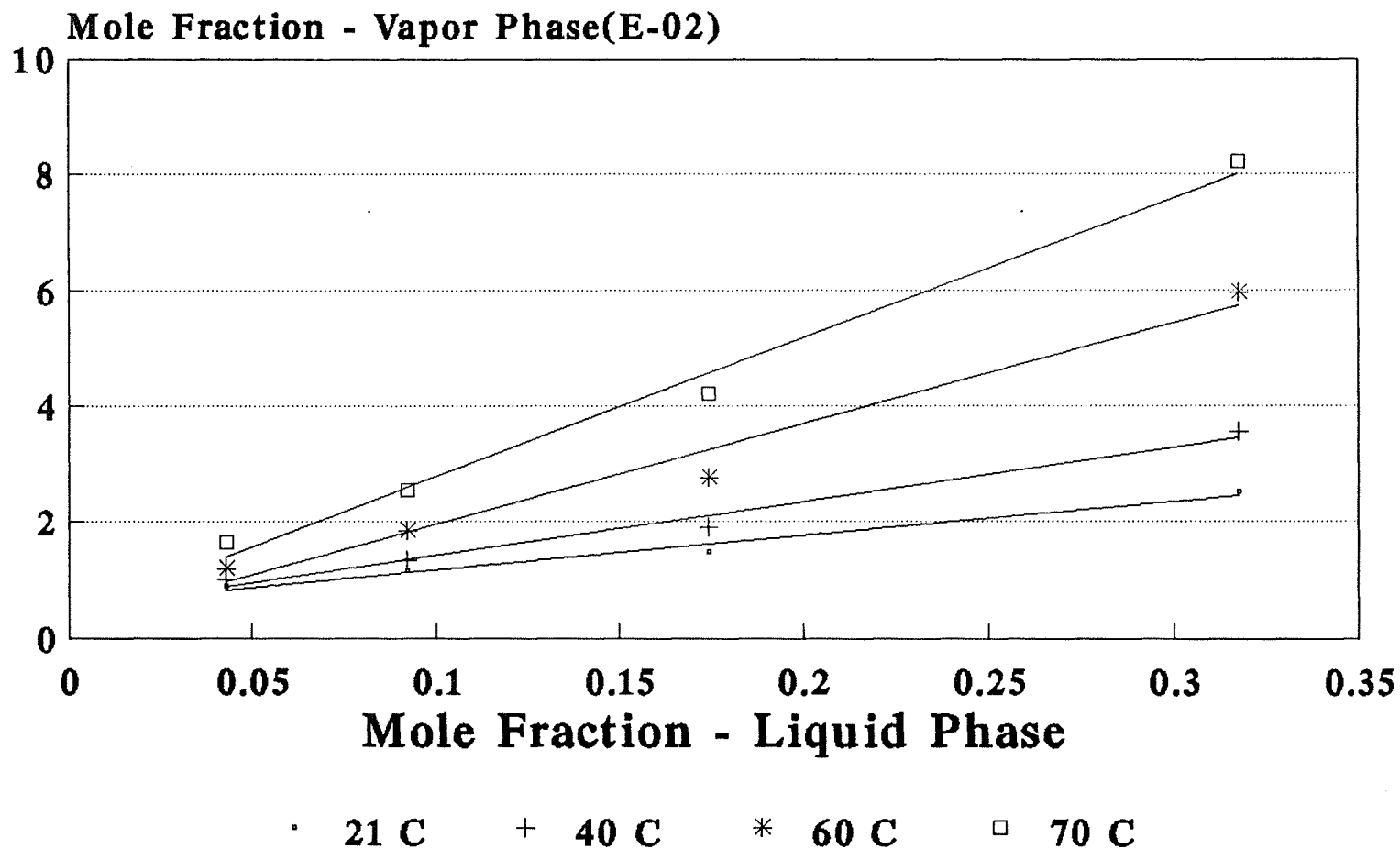
Fig. IV--12 TOLUENE MOLE FRACTION
Surfactant: Sodium Sulfonate
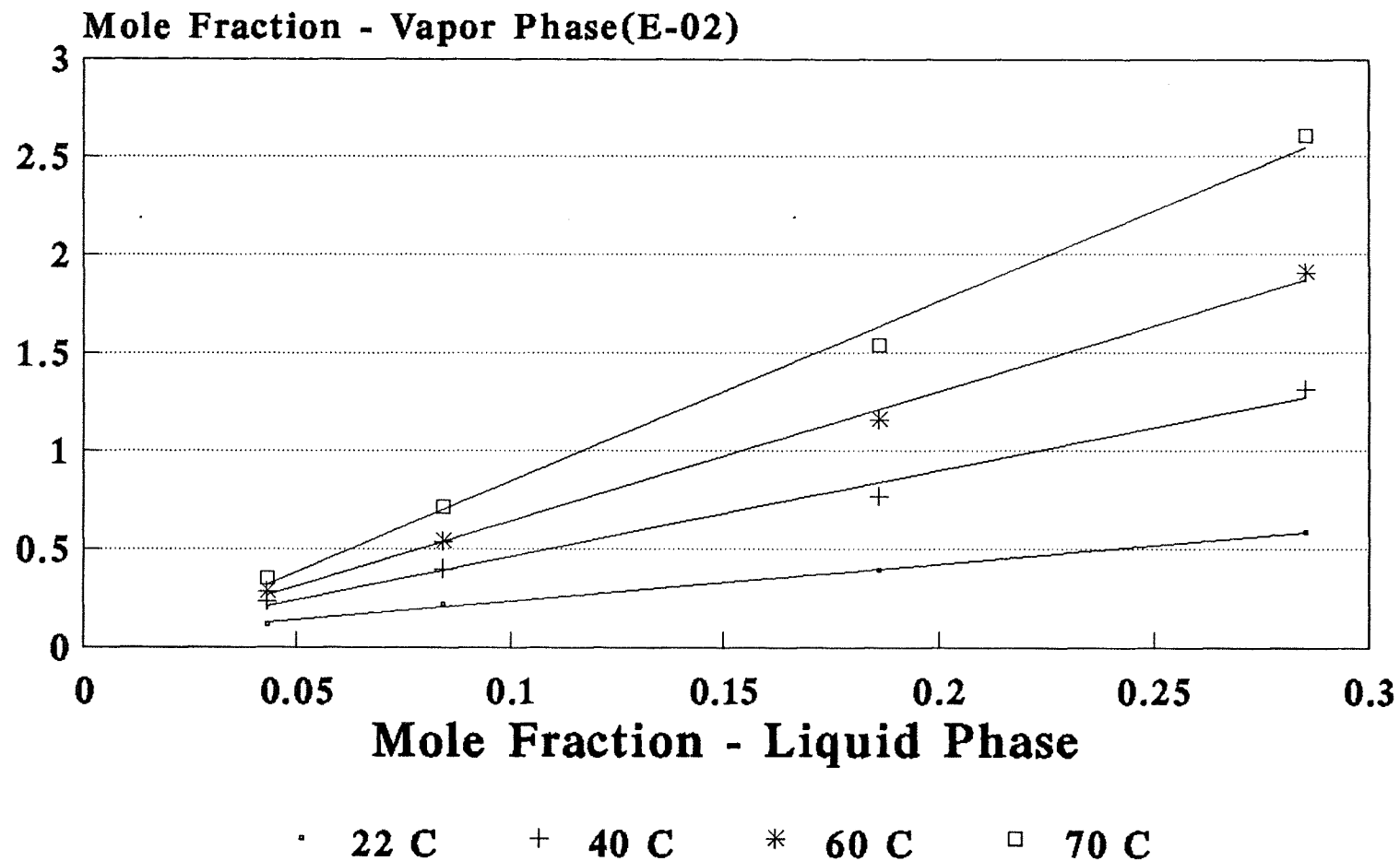
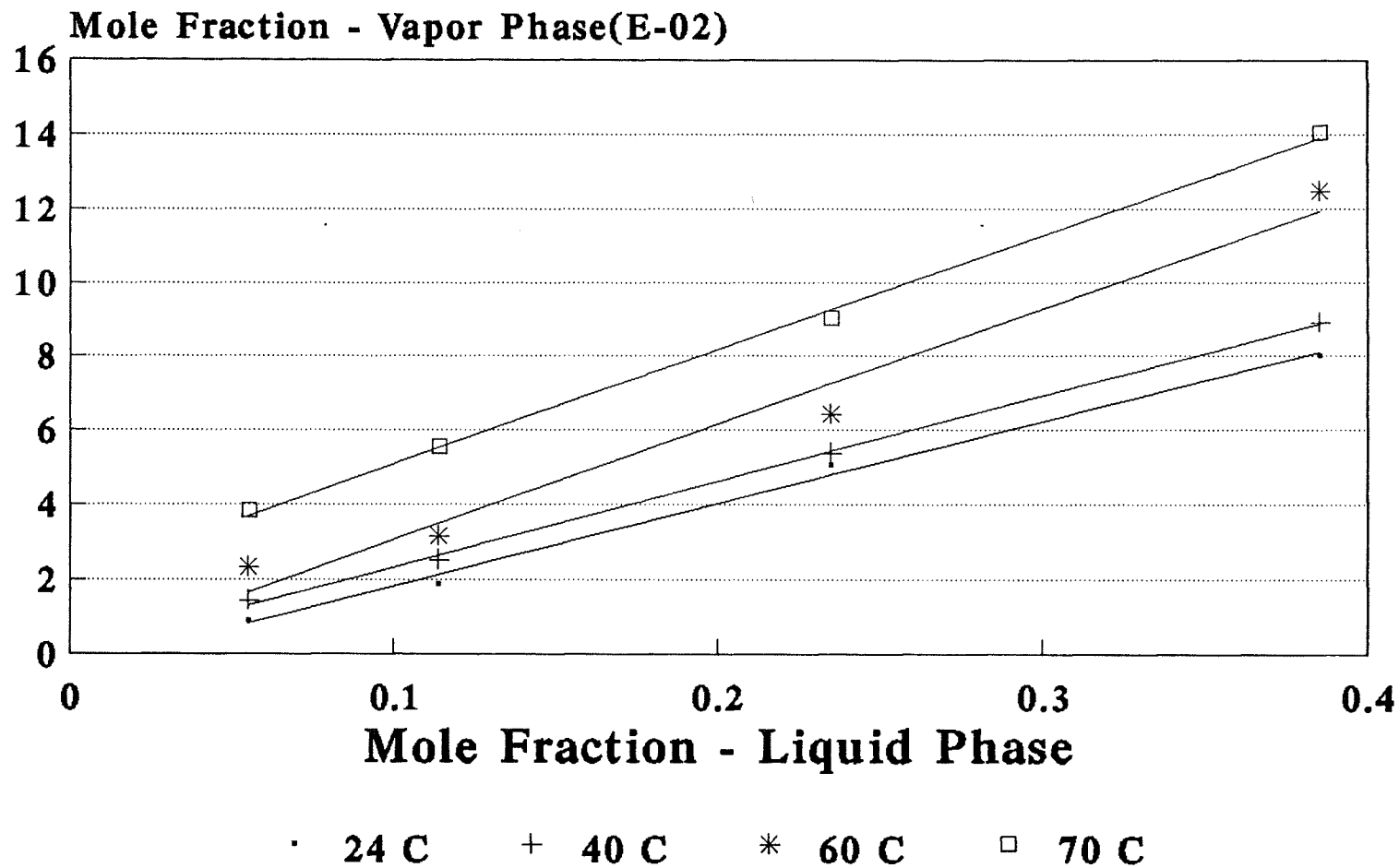# Fig. IV--13 BUTYL ACETATE MOLE FRACTION
Surfactant: Sodium Sulfonate

Mole Fraction - Vapor Phase(E-02)

Mole Fraction - Liquid Phase

· 22 C   + 40 C   * 60 C   □ 70 C
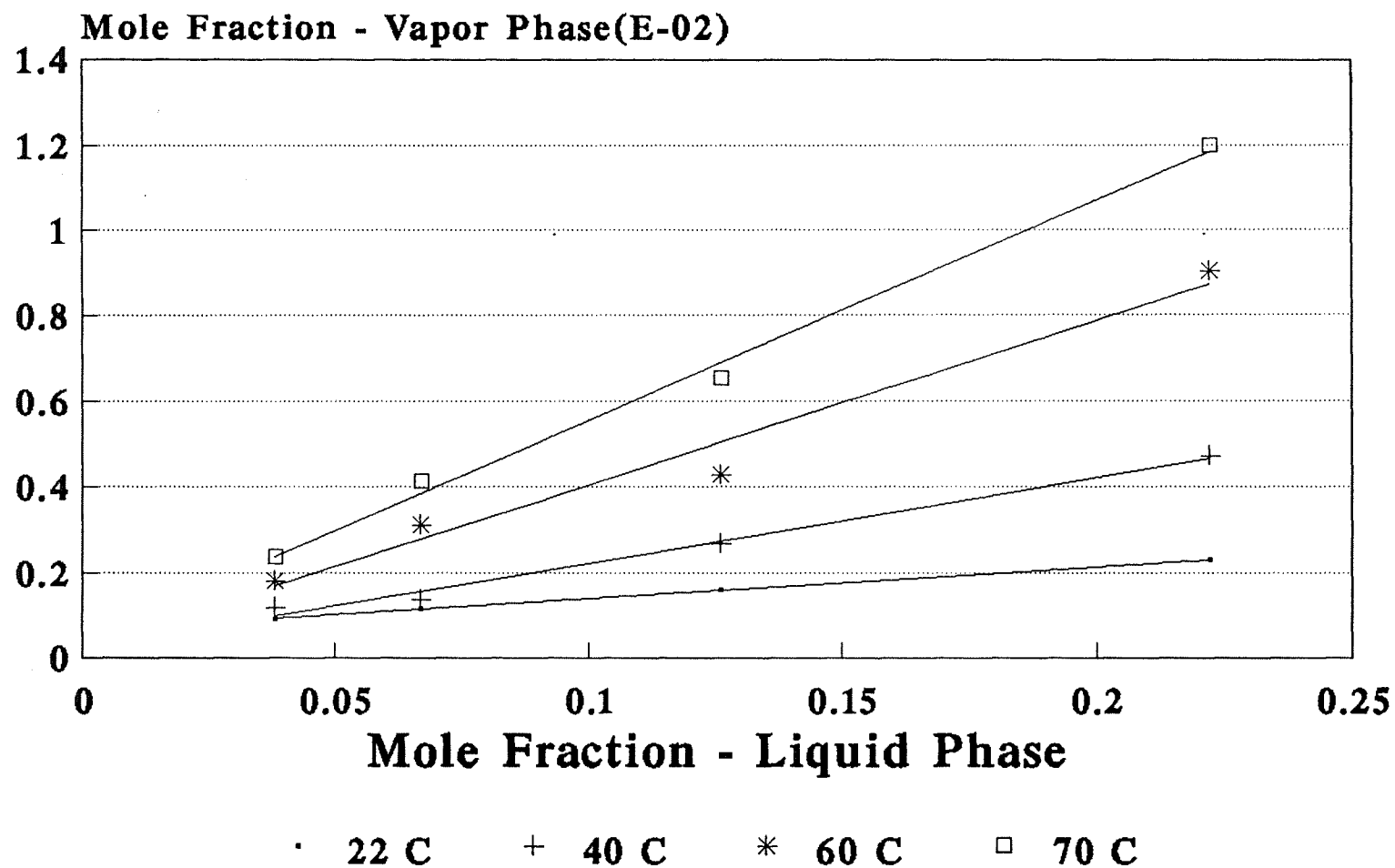
Fig. IV--14 ACETONE MOLE FRACTION
Surfactant: Sodium Sulfonate

Mole Fraction - Vapor Phase(E-02)

Mole Fraction - Liquid Phase

· 24 C   + 40 C   * 60 C   □ 70 C

Fig. IV--15 i-PROPANOL MOLE FRACTION
Surfactant: Sodium Sulfonate

Mole Fraction - Vapor Phase(E-02)

Mole Fraction - Liquid Phase

· 24 C   + 40 C   * 60 C   □ 70 C
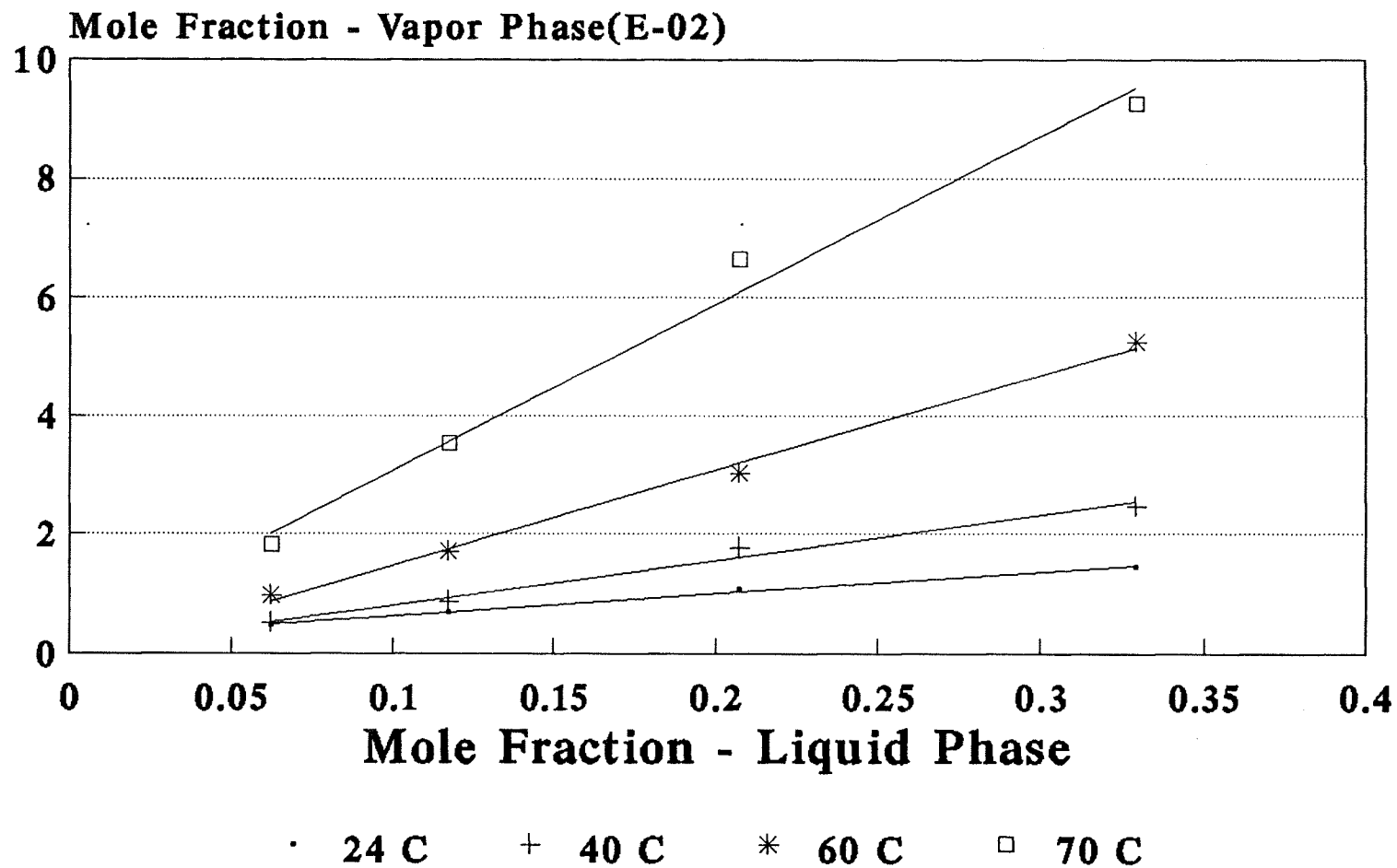
Fig. IV--16 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (22 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· MEK   —+— Toluene   —*— Butyl Acetate   —□— Acetone   × i-propanol
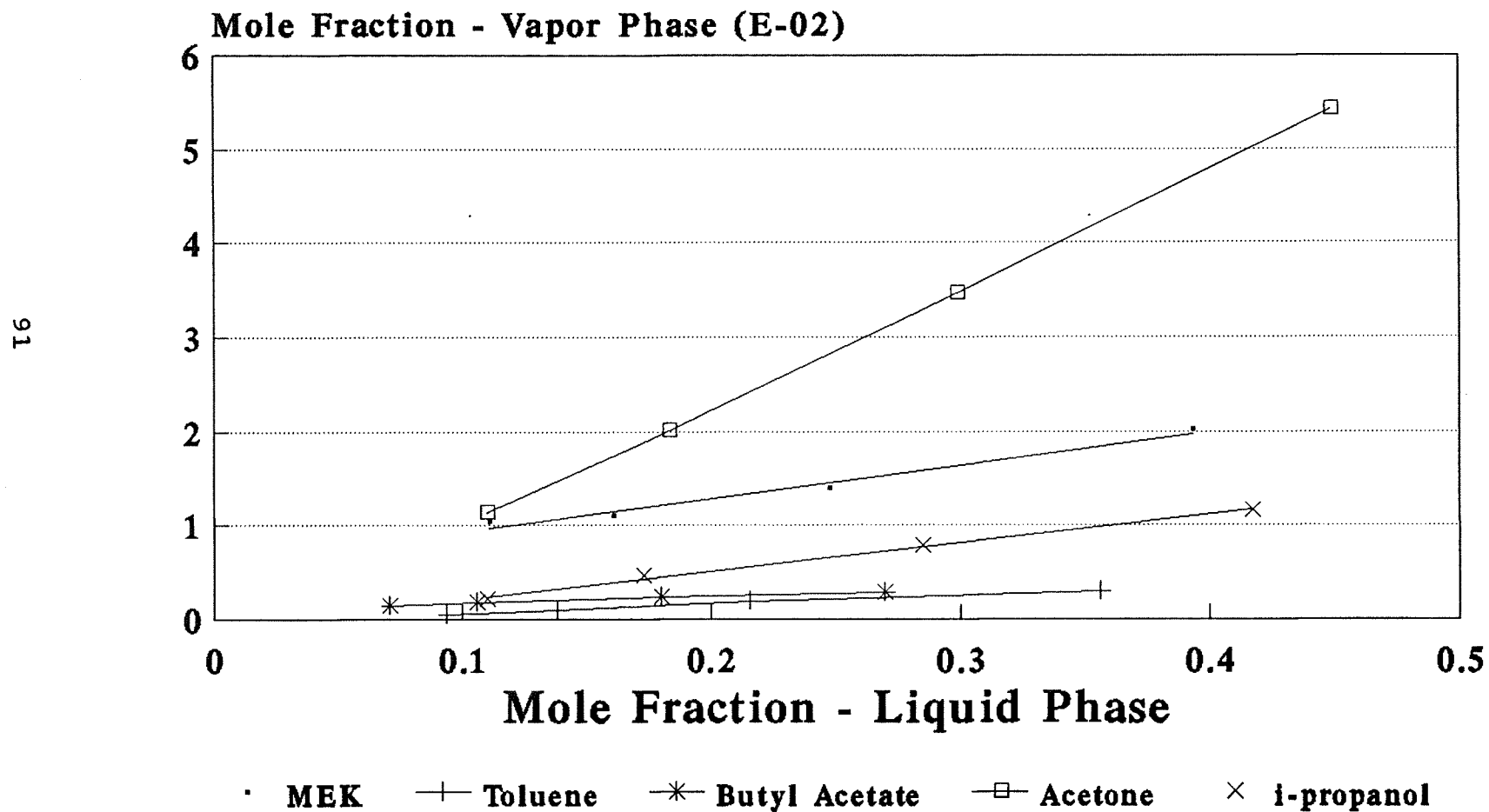
Surfactant: Octylphenyl Decaethoxylate

Fig. IV--17 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (40 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· MEK   —+— Toluene   —*— Butyl Acetate   □ Acetone   × i-propanol
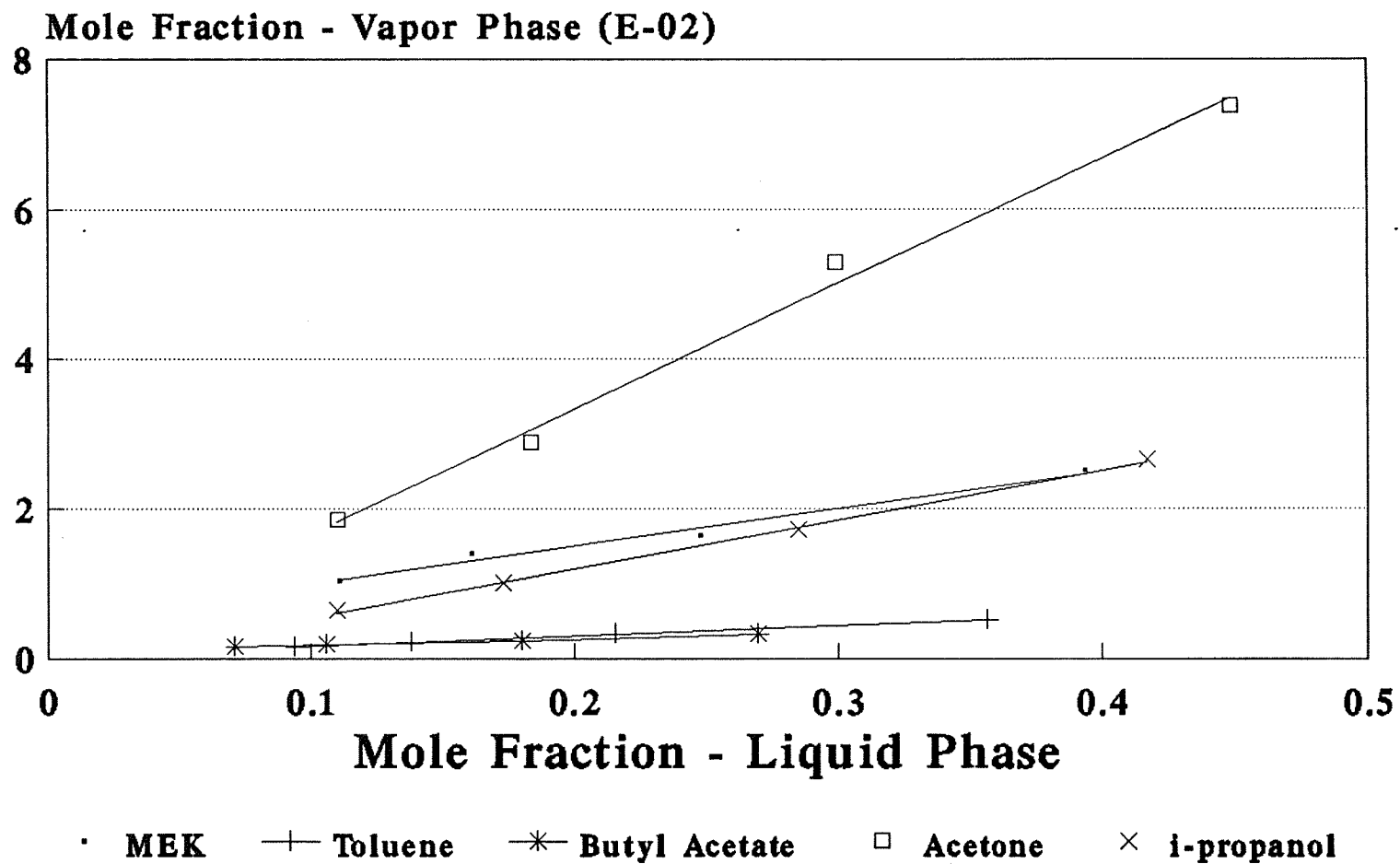
Surfactant: Octylphenyl Decaethoxylate

Fig. IV--18 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (60 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

- MEK
□ Acetone
—+— Toluene
× i-propanol
—*— Butyl Acetate
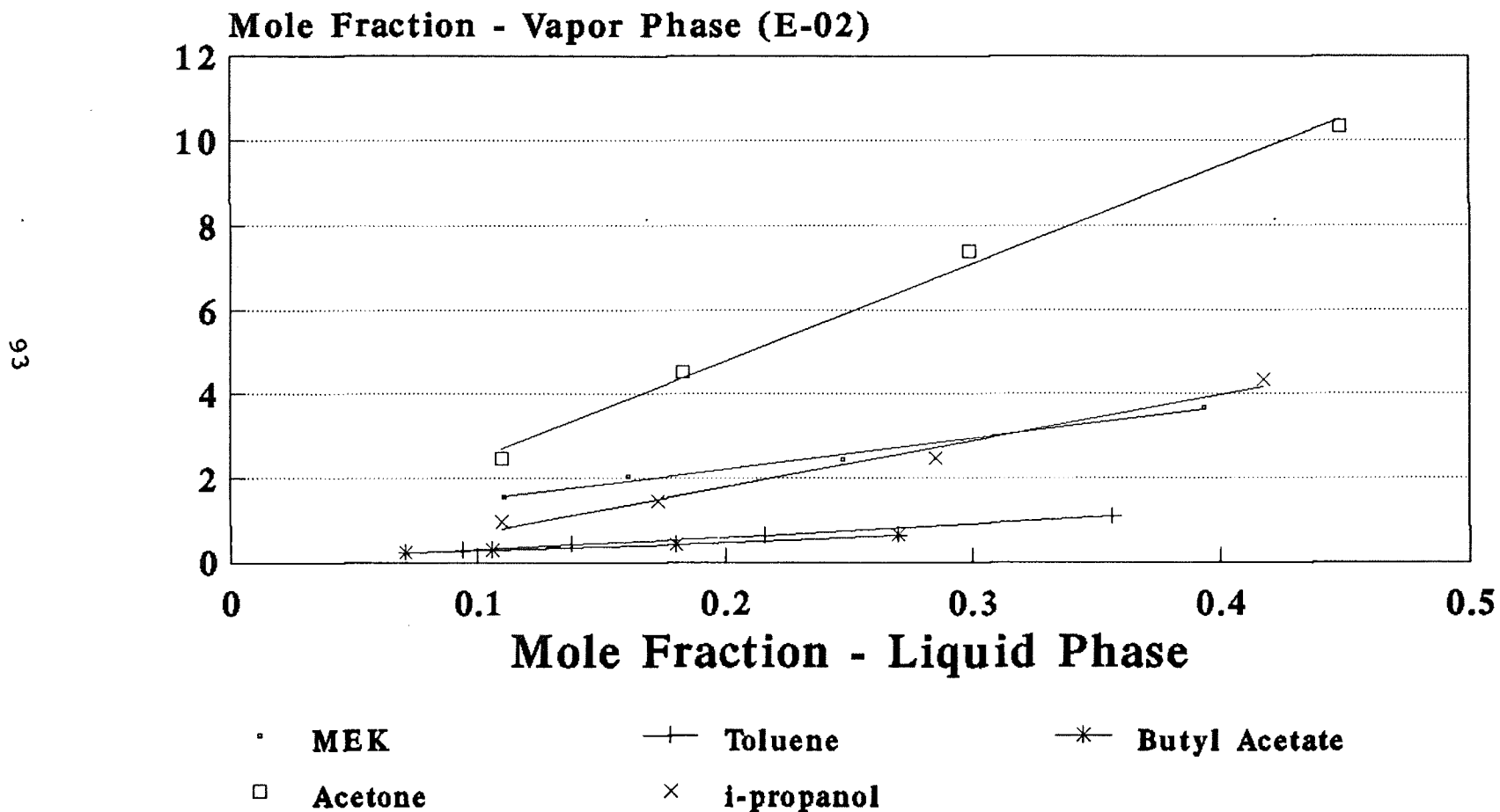
Surfactant: Octylphenyl Decaethoxylate

Fig. IV--19 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (70 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

- • MEK
- □ Acetone
- + Toluene
- × i-propanol
- * Butyl Acetate

Surfactant: Octylphenyl Decaethoxylate

94
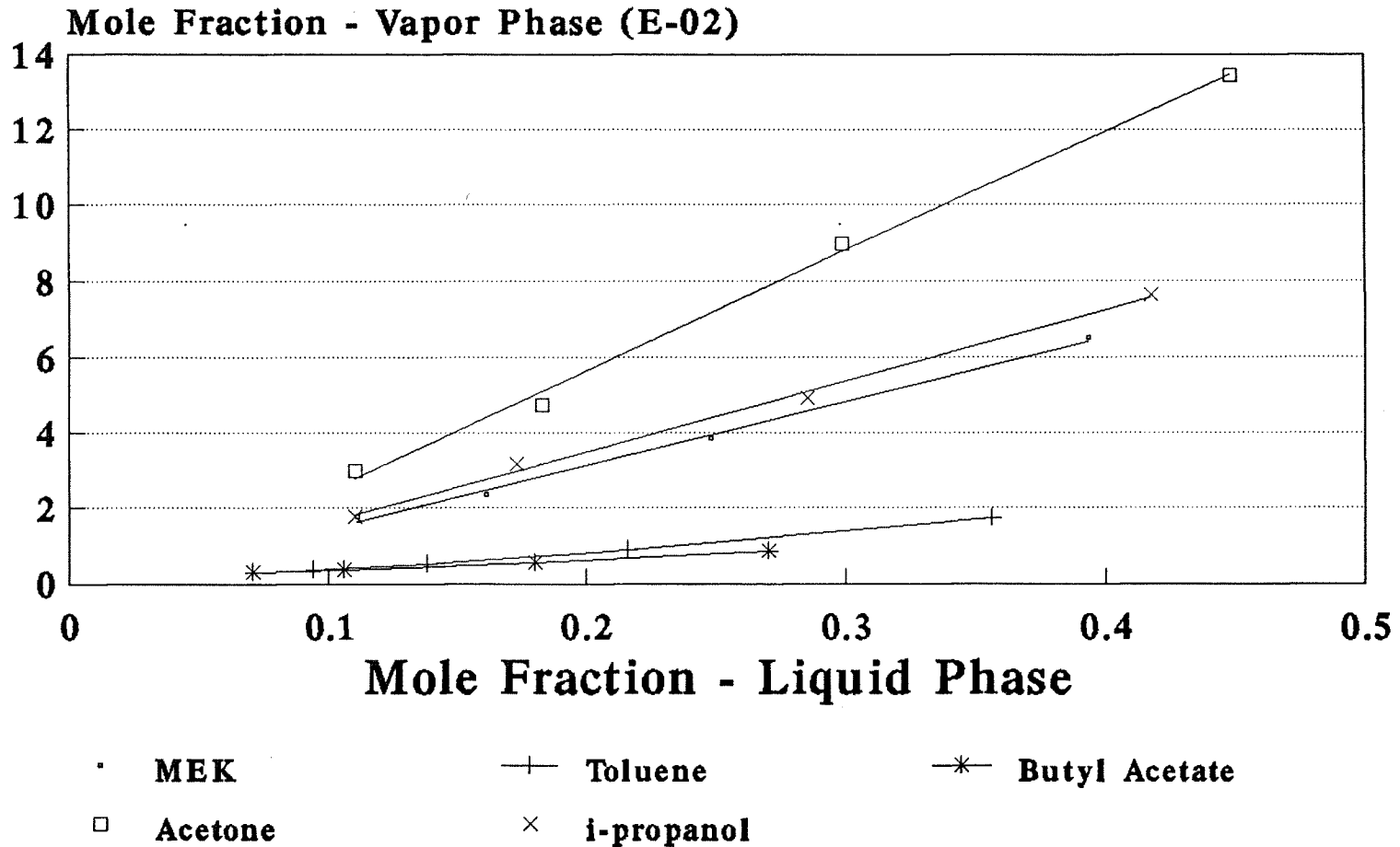
Fig. IV--20 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (22 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

—— Toluene   —+— Butyl Acetate   * i-propanol   □ Acetone   × MEK
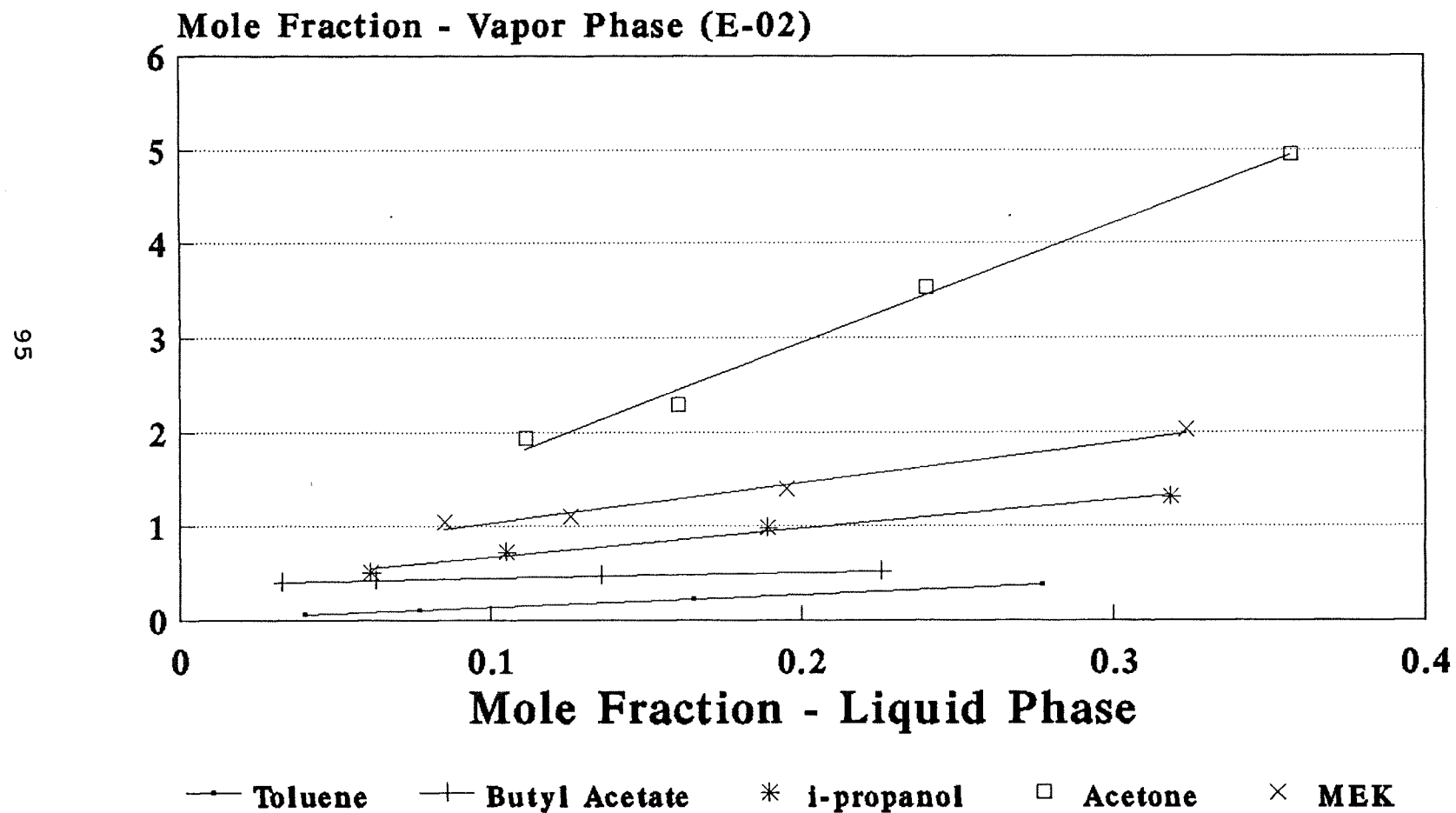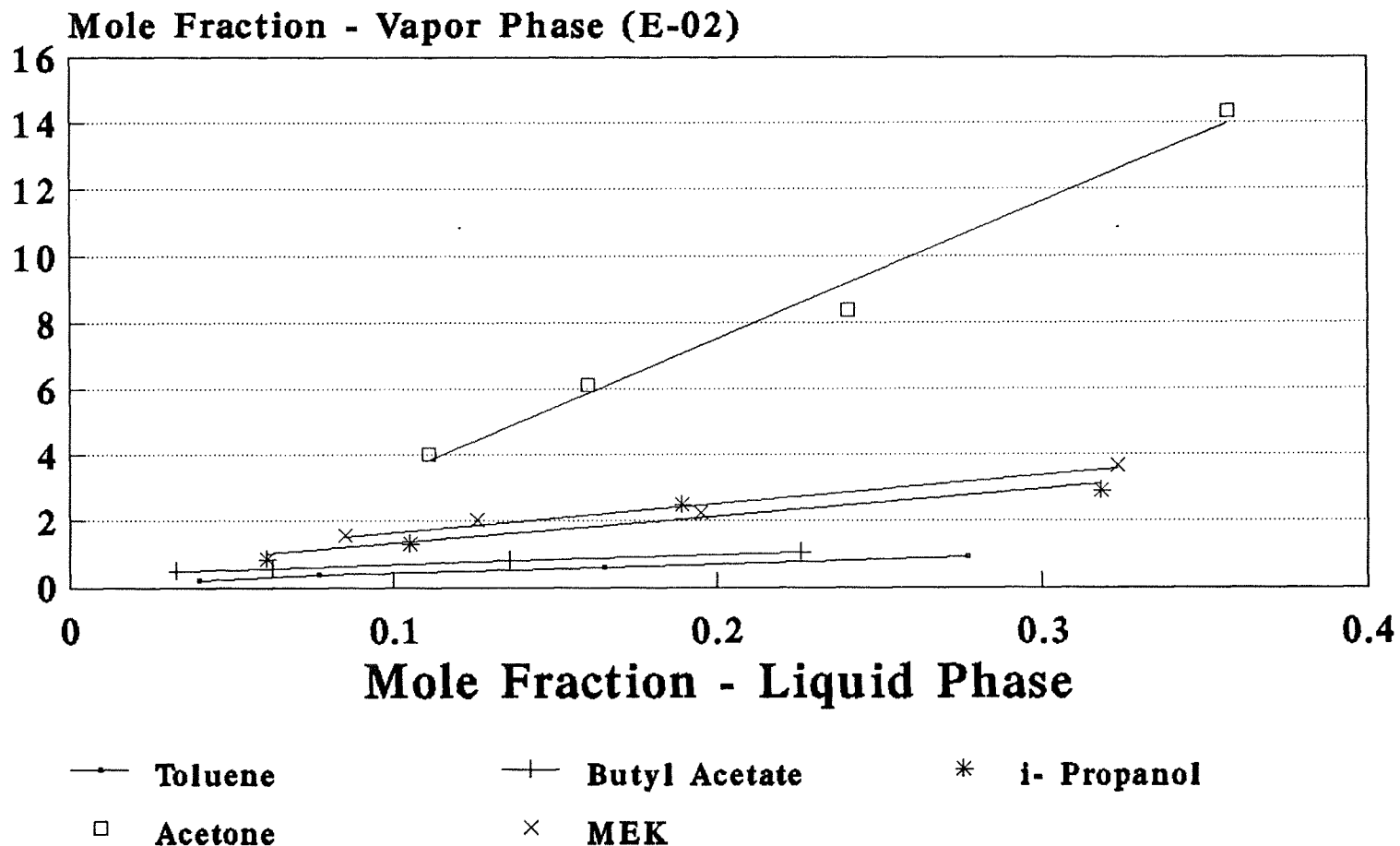
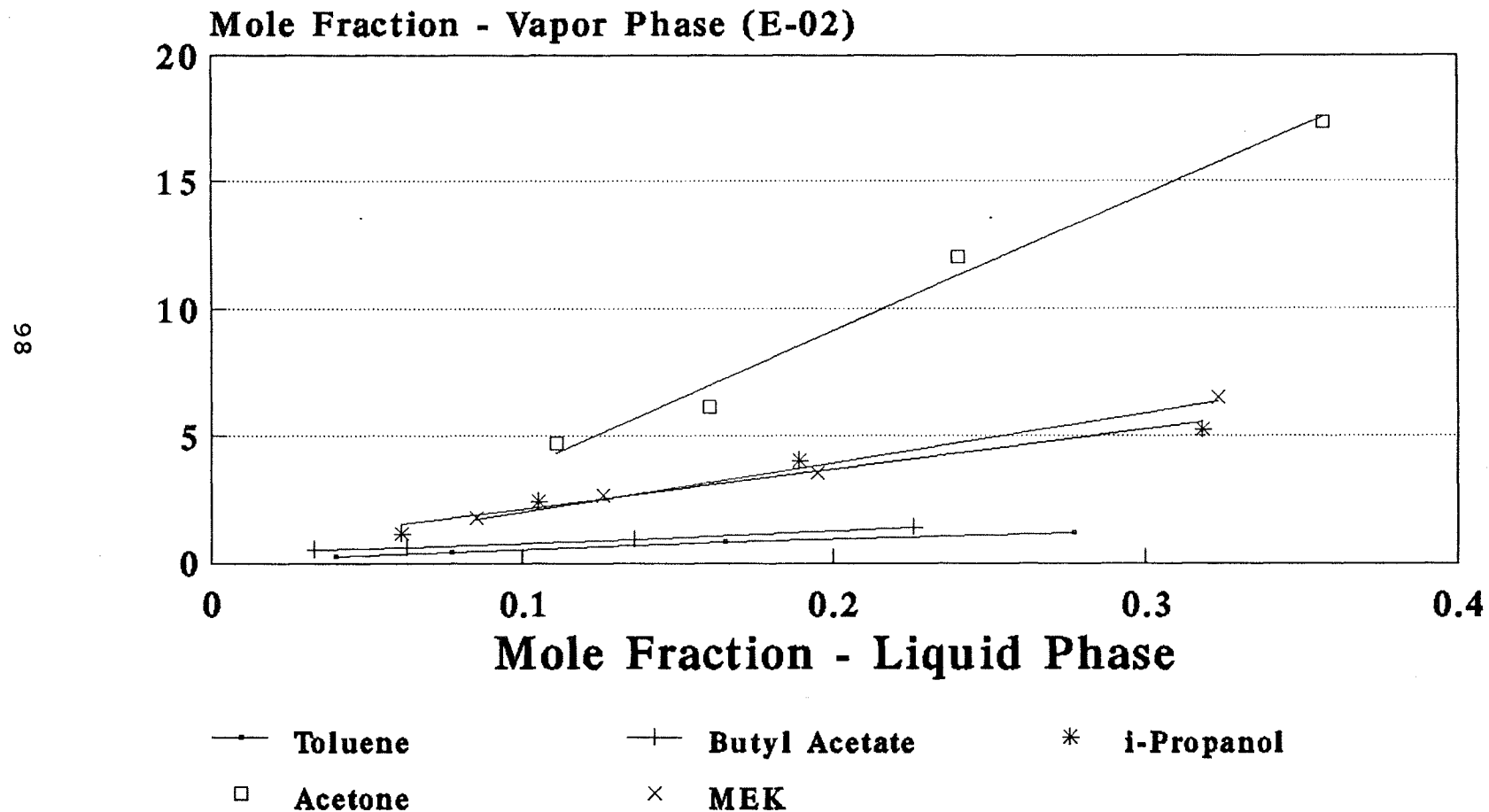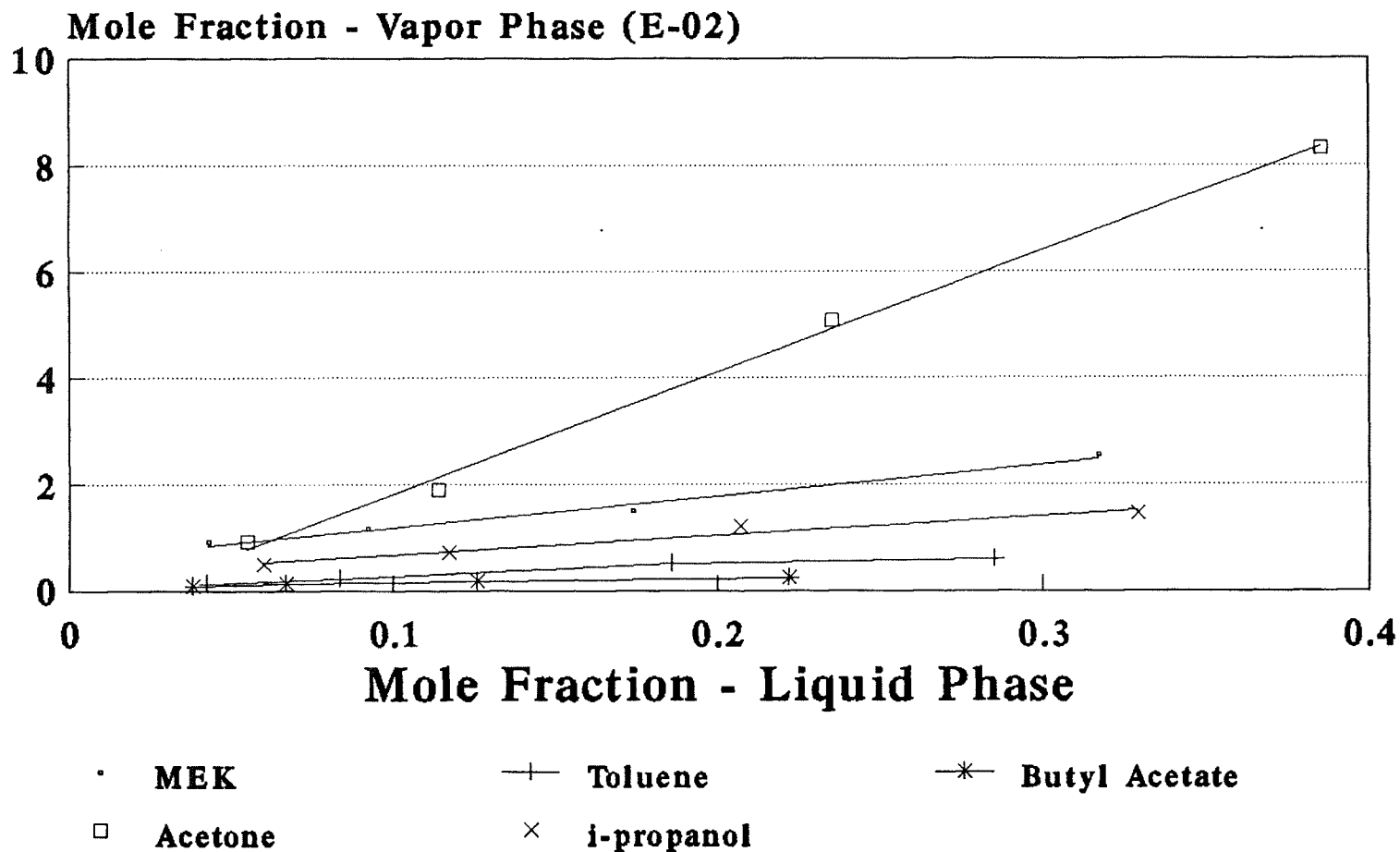Surfactant: Sorbitan Monooleate

Fig. IV--21 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (40 C)
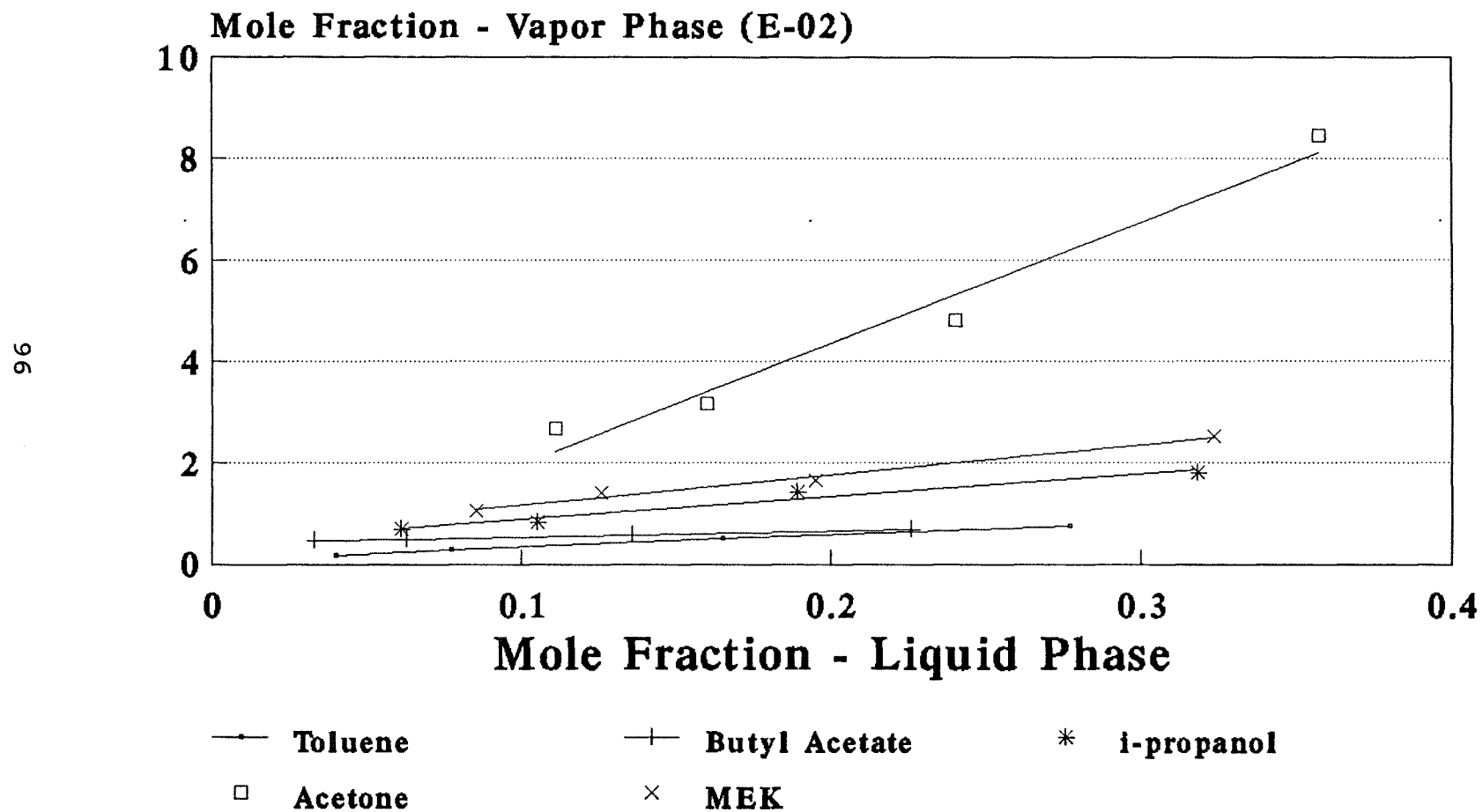
Surfactant: Sorbitant Monooleate

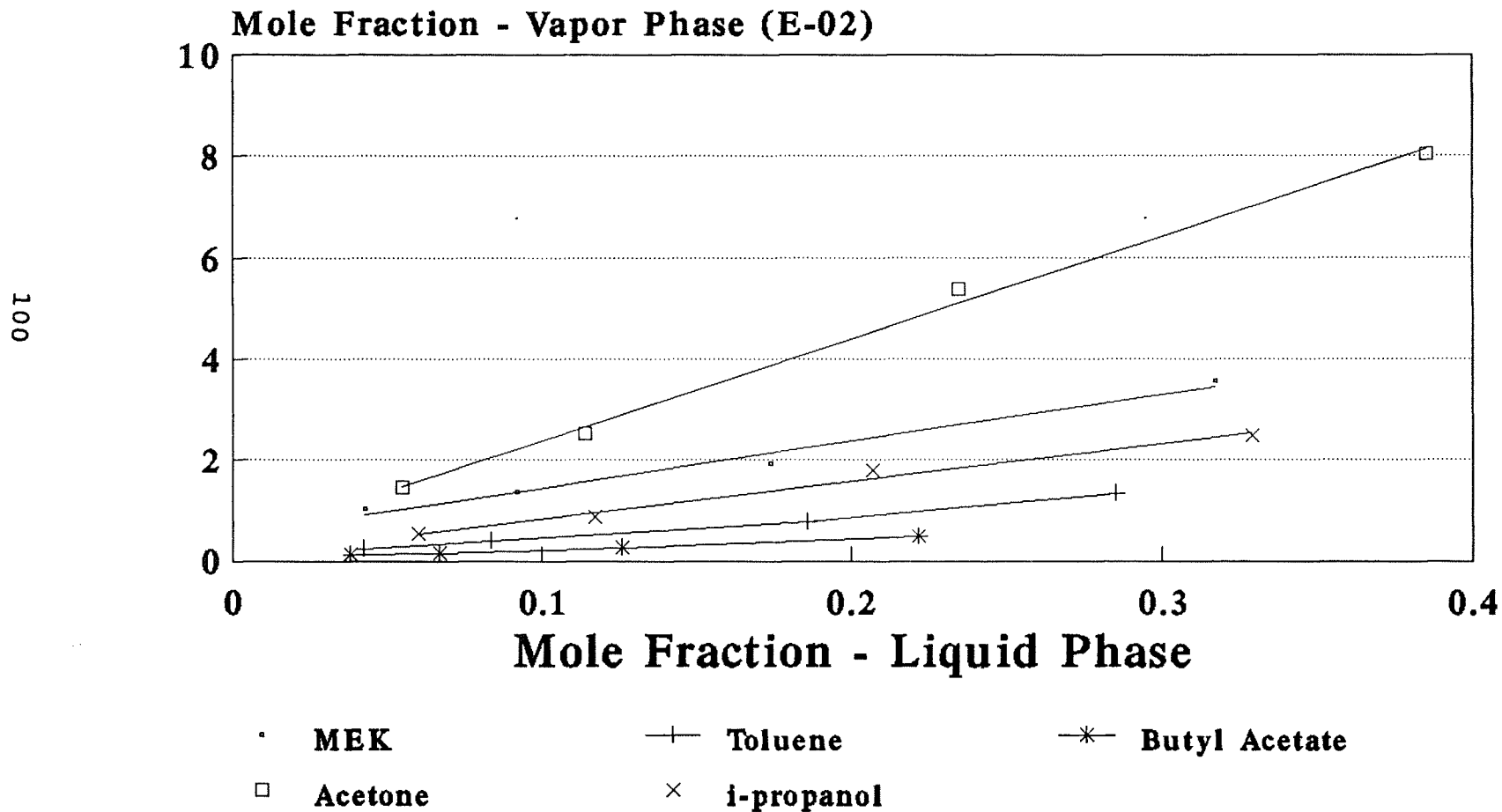# Fig. IV--22 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (60 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

— Toluene   —|— Butyl Acetate   * i- Propanol

□ Acetone   × MEK

Surfactant: Sorbitan Monoolete

Fig. IV--23 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (70 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

— Toluene   —+— Butyl Acetate   * i-Propanol

□ Acetone   × MEK

Surfactant: Sorbitan Monooleate

Fig. IV--24 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (22 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· MEK   —+— Toluene   —*— Butyl Acetate

□ Acetone   × i-propanol

Surfactant: Sodium Sulfonate

Fig. IV--25 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (40 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

- MEK
□ Acetone
─+─ Toluene
× i-propanol
─*─ Butyl Acetate

Surfactant: Sodium Sulfonate

Fig. IV--26 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (60 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· MEK   —|— Toluene   —*— Butyl Acetate

□ Acetone   × i-propanol
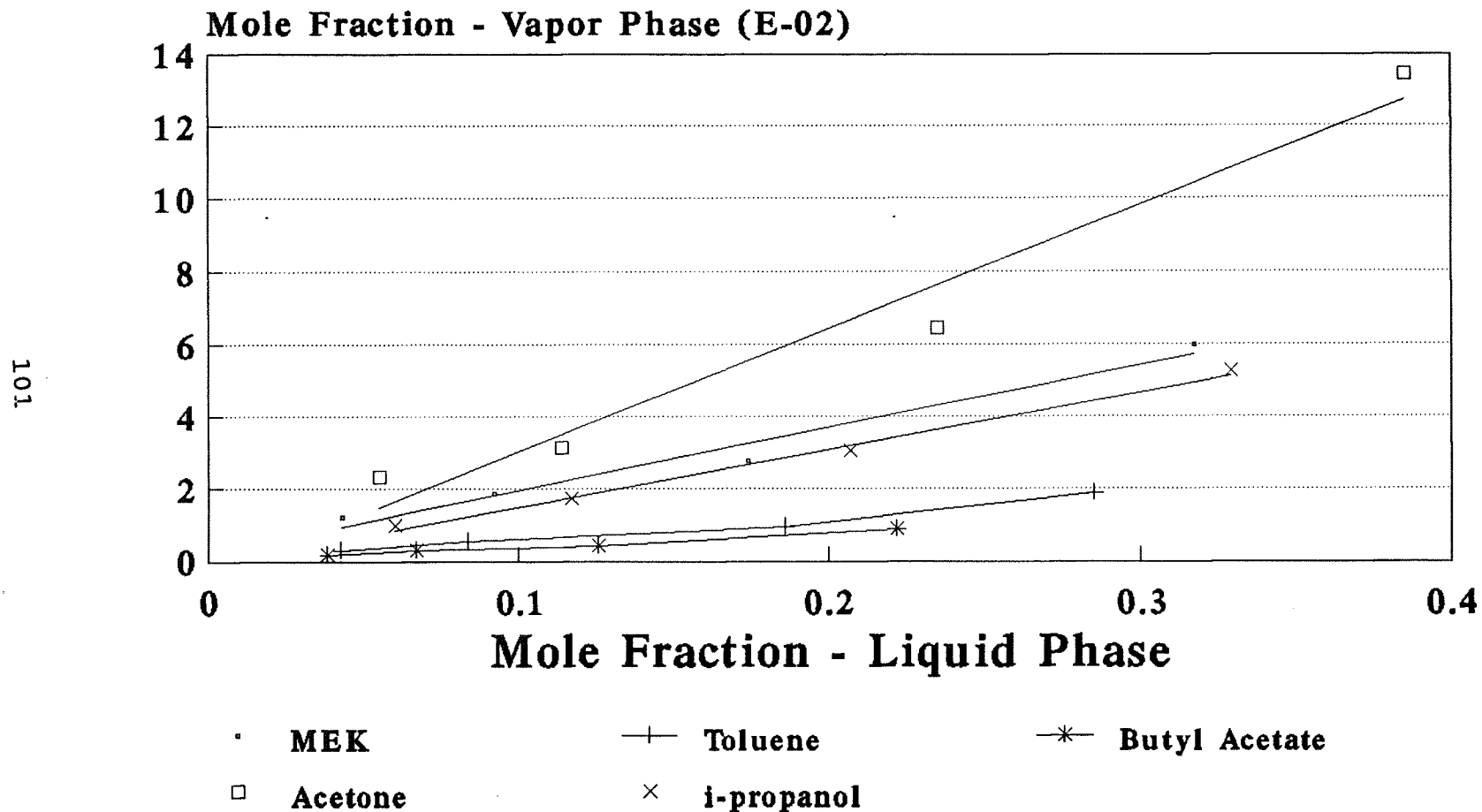
Surfactant: Sodium Sulfonate

Fig. IV--27 VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION (70 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

- • MEK
- —+— Toluene
- —*— Butyl Acetate
- □ Acetone
- × i-propanol

Surfactant: Sodium Sulfonate

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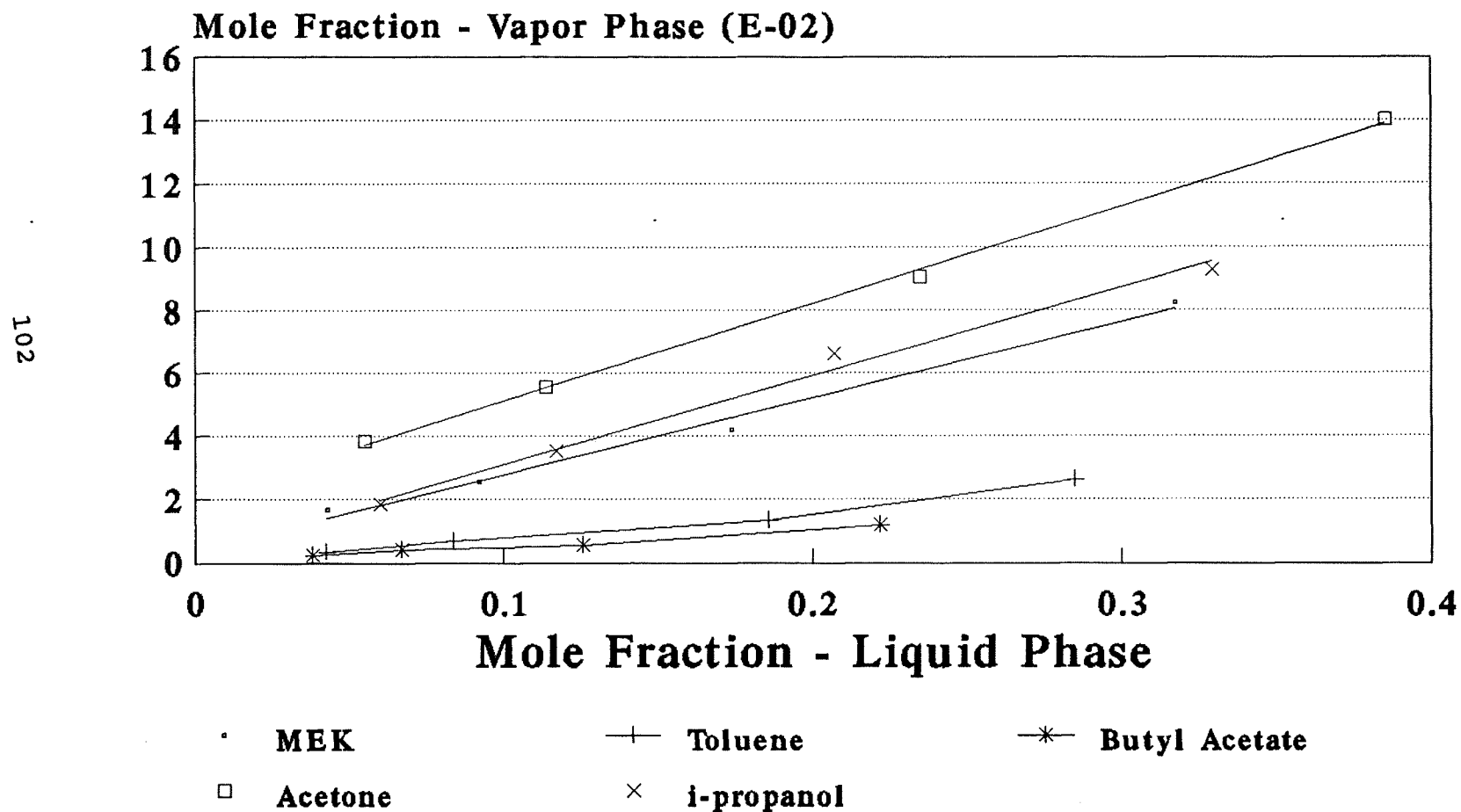
Fig.IV-28 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF MEK (22 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate
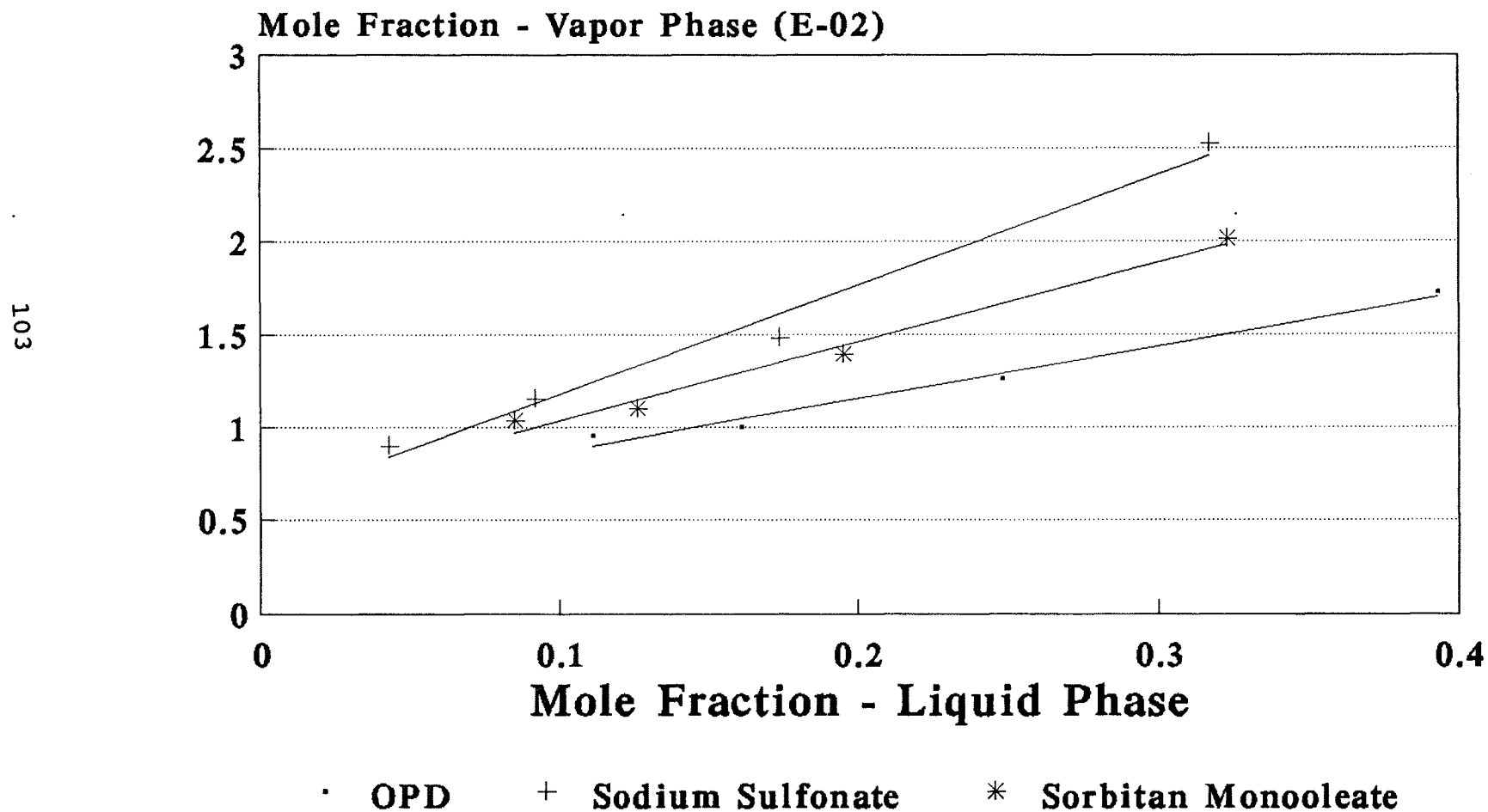
Fig.IV-29 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF MEK (40 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate
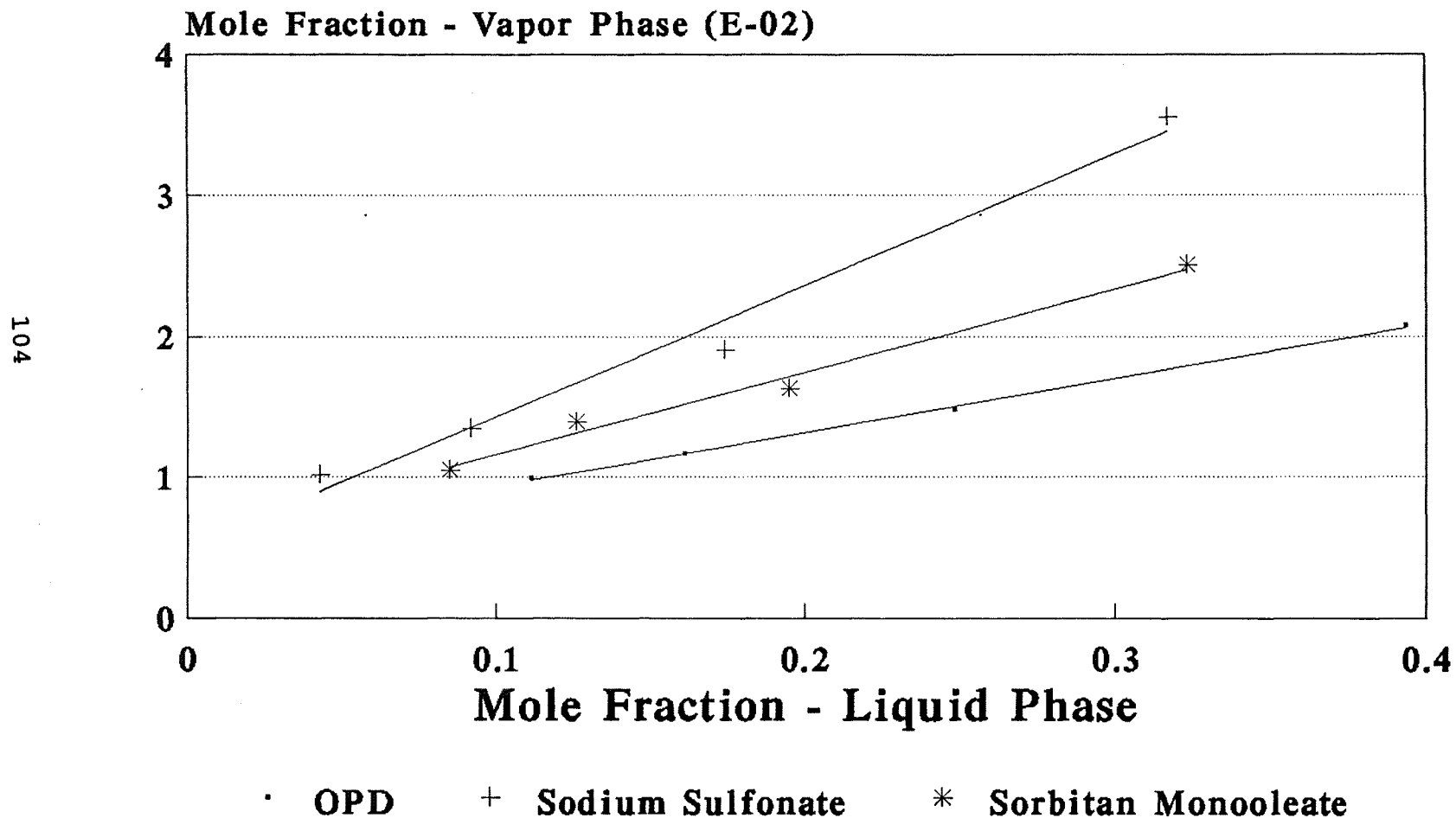
Fig.IV-30 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF MEK (60 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate
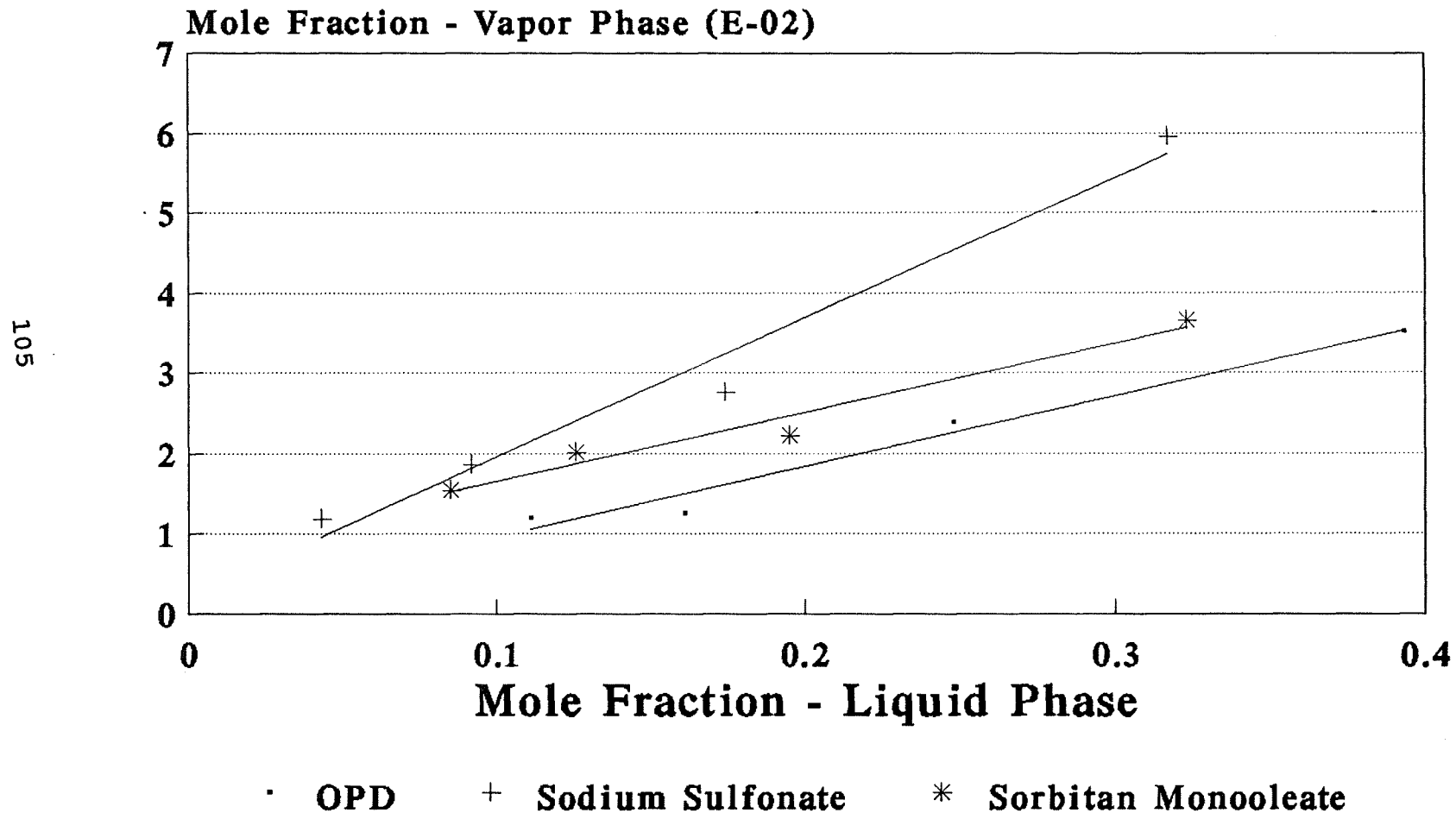
Fig.IV-31 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF MEK (70 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate
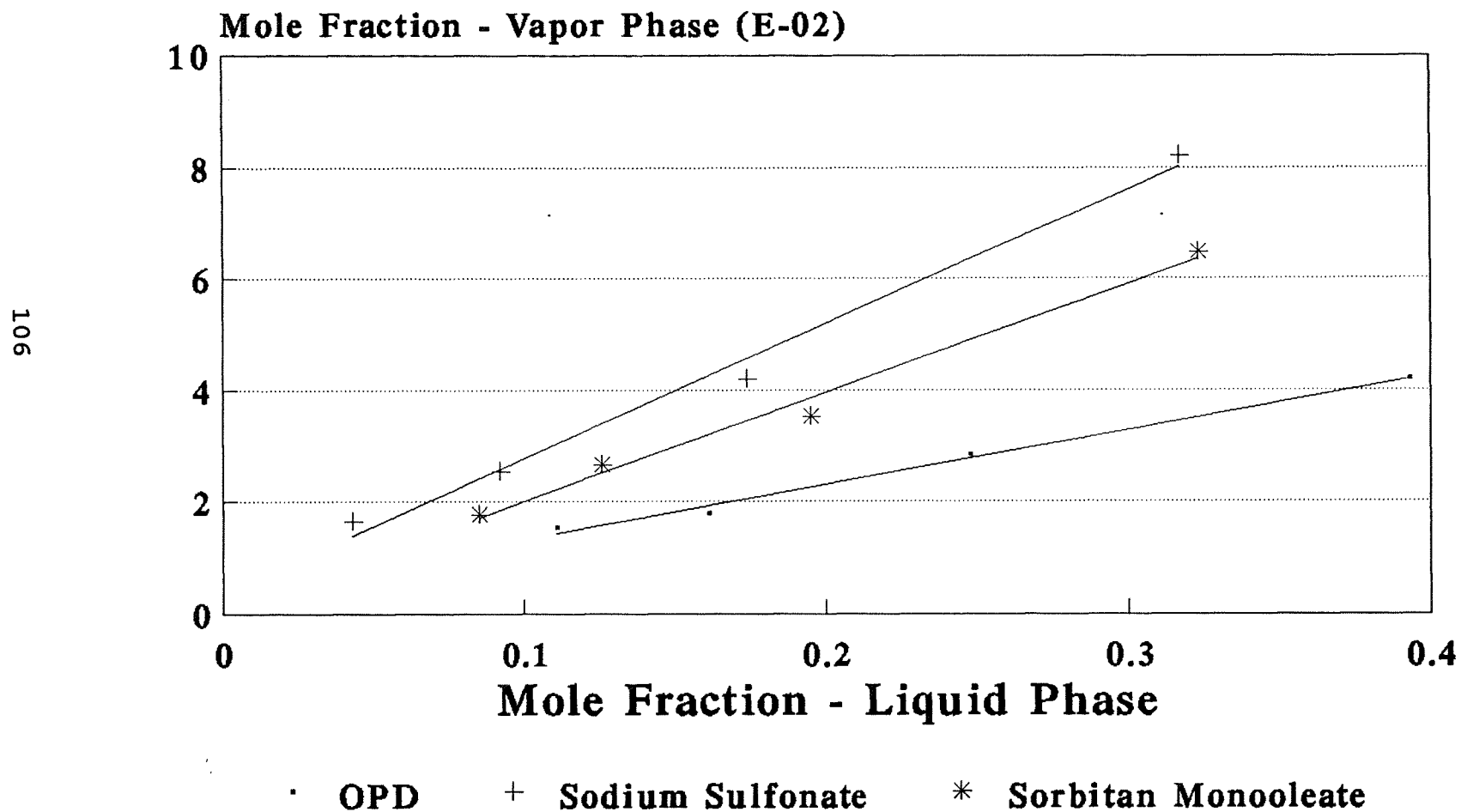
Fig.IV-32 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF TOLUENE (22 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase
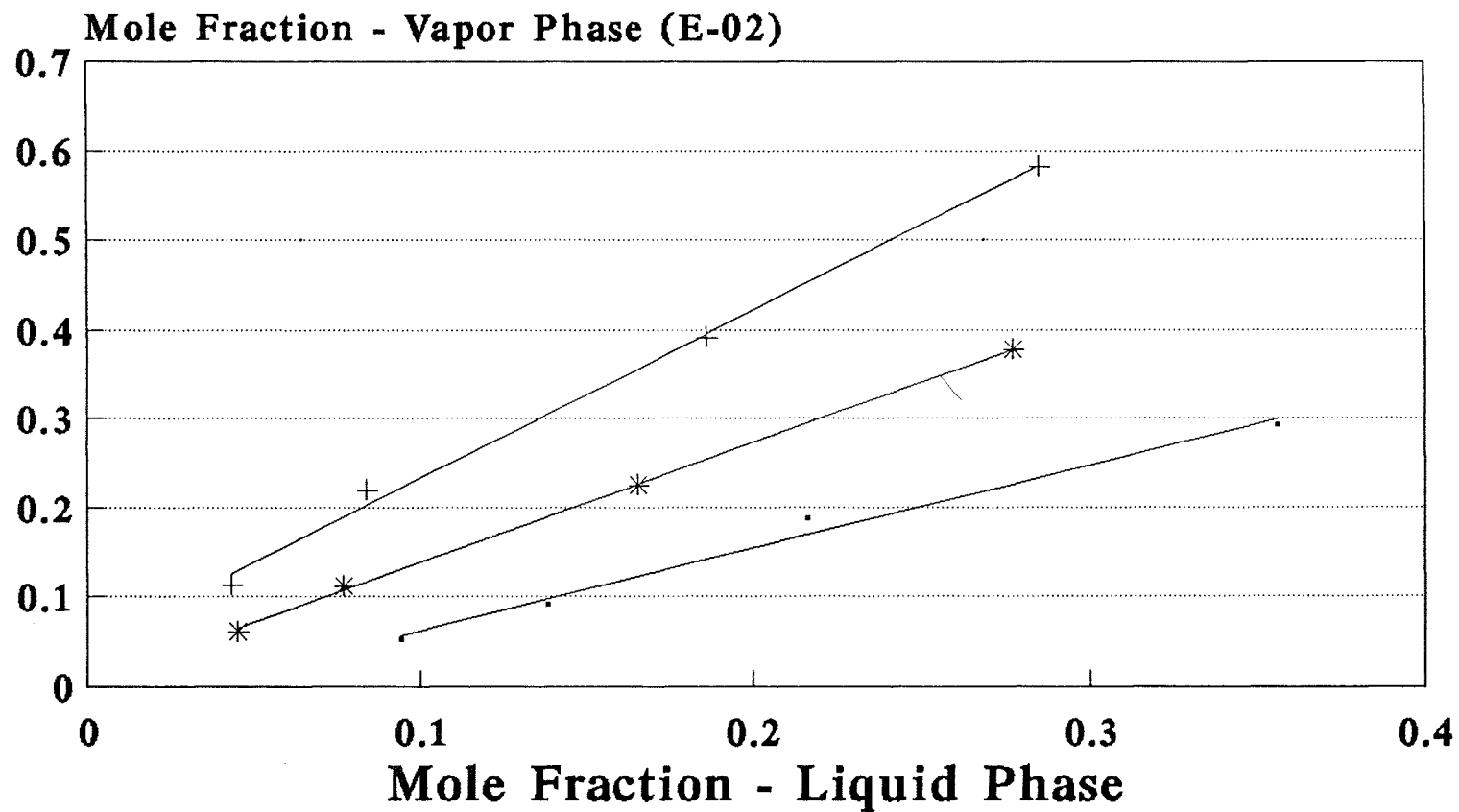
· OPD   + Sodium Sulfonate   * Sorbitan Monooleate

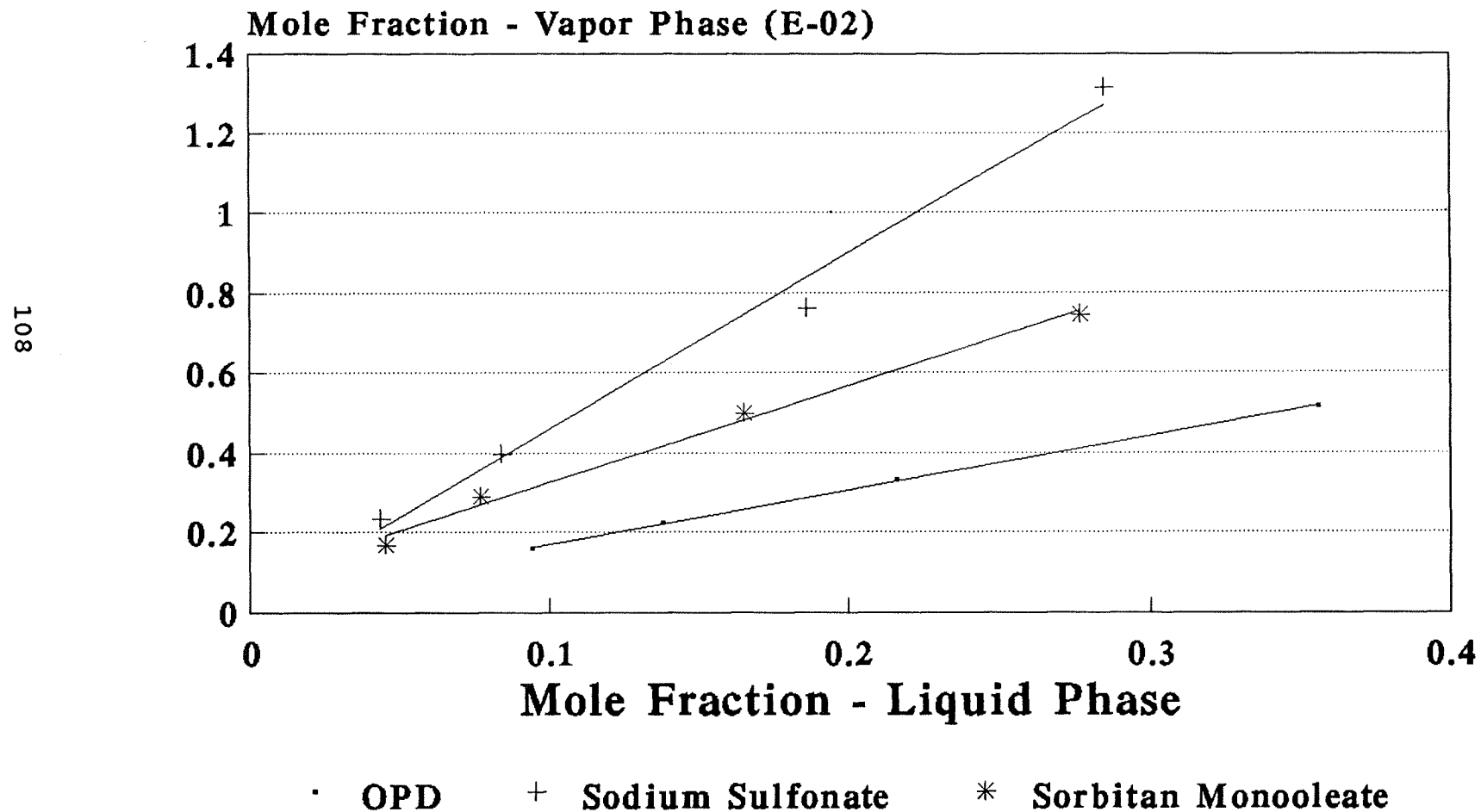# Fig.IV-33 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF TOLUENE (40 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate

Fig.IV-34 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF TOLUENE (60 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate

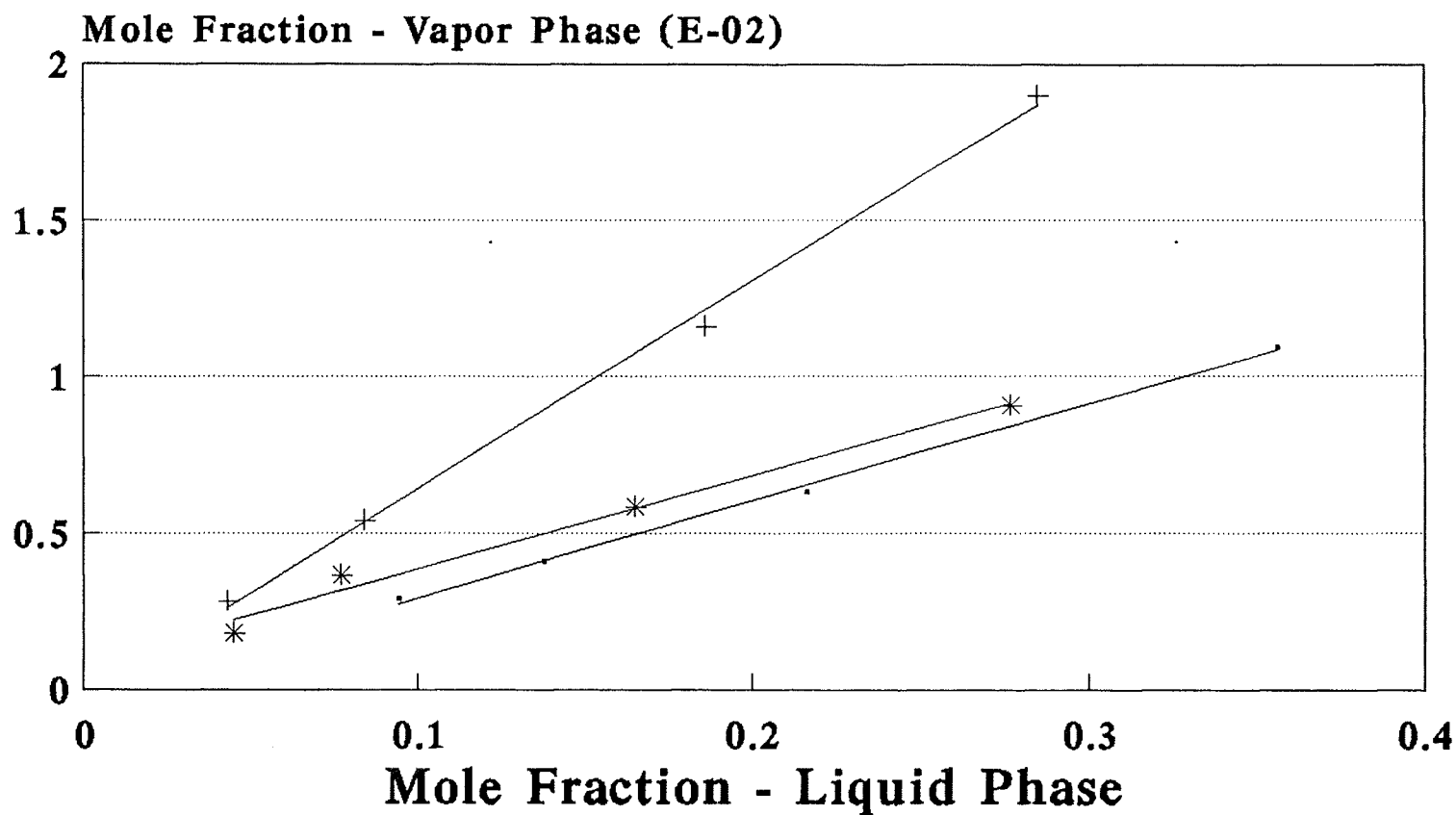# Fig.IV-35 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF TOLUENE (70 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate

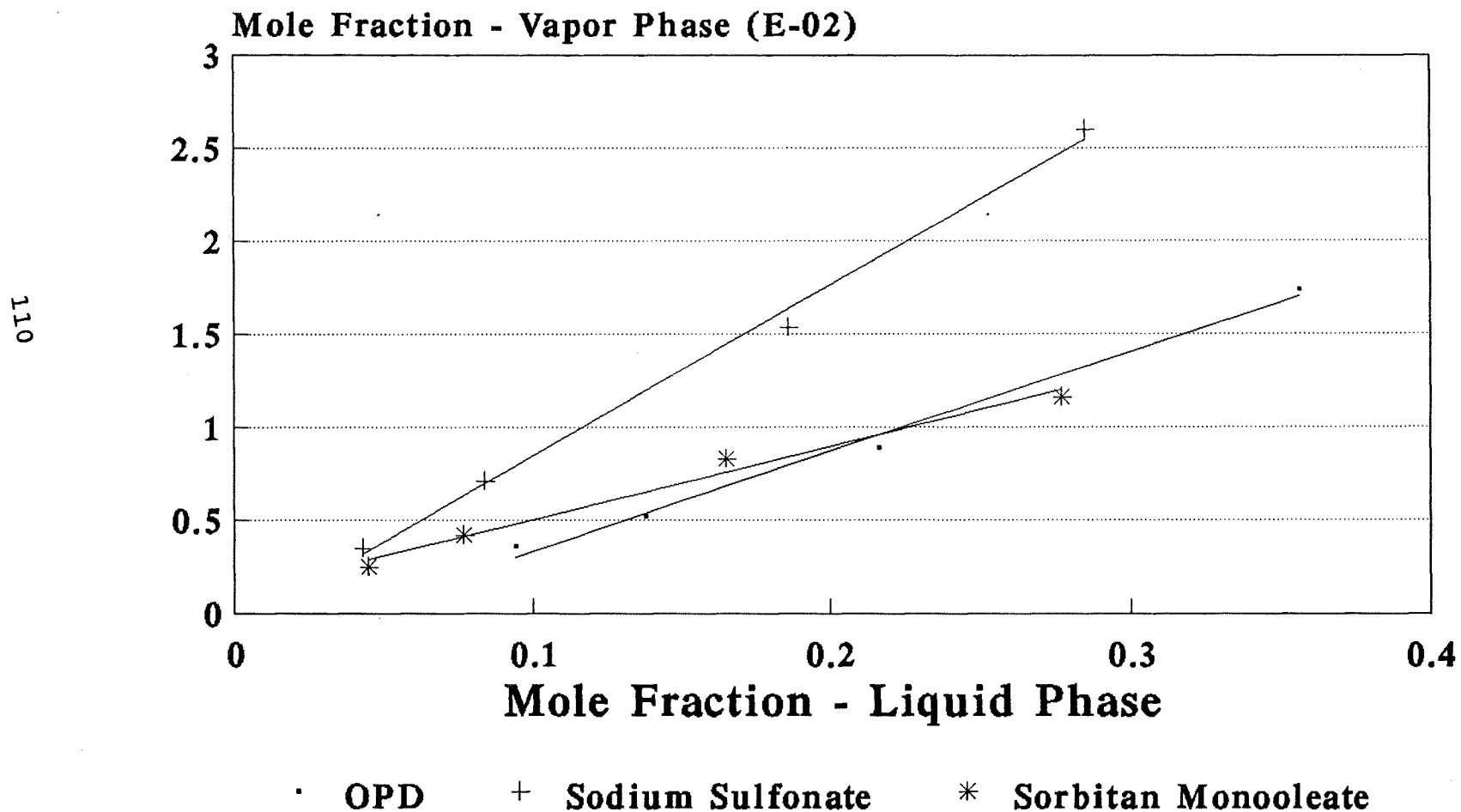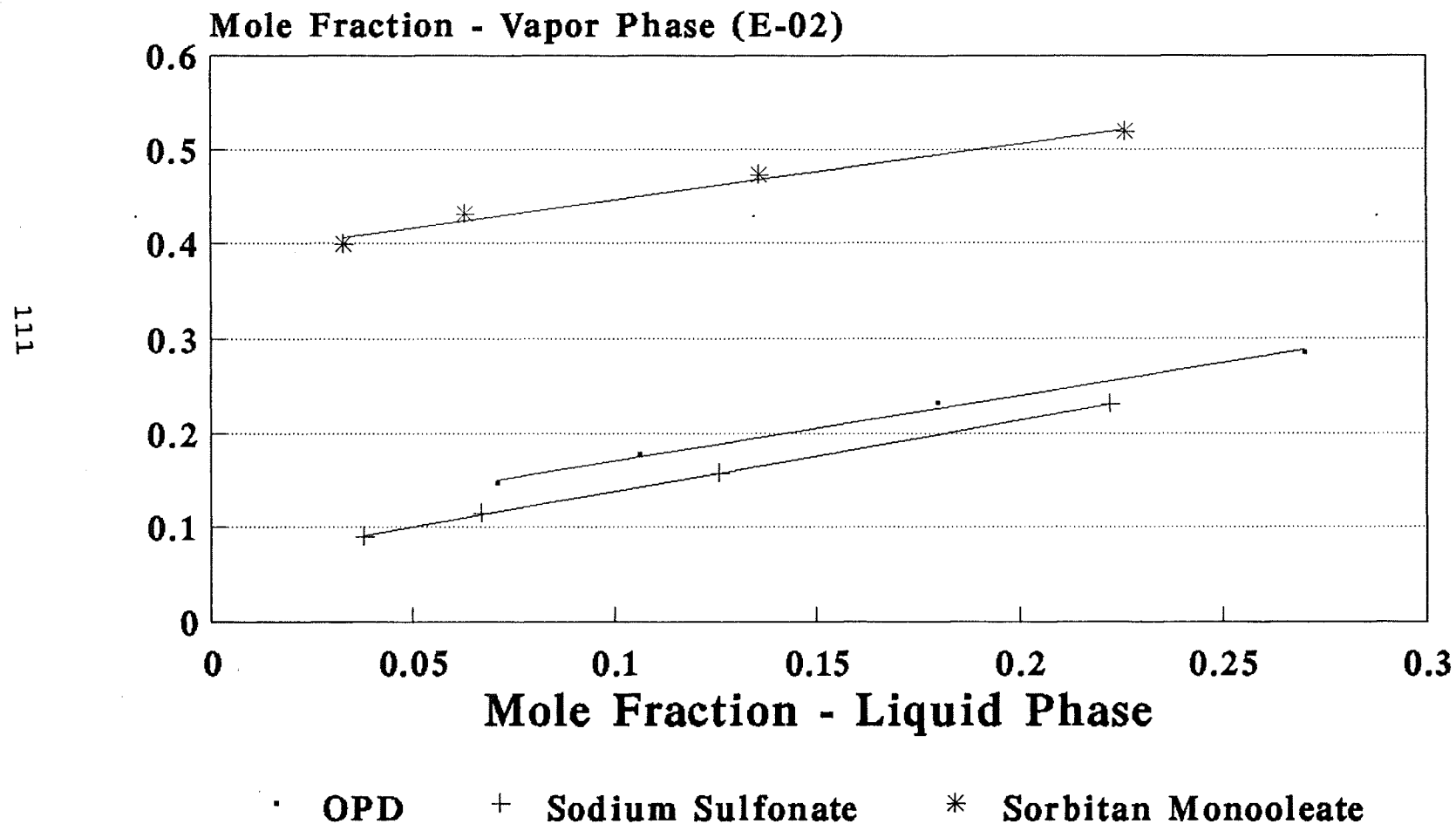# Fig.IV-36 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF B.A.*(22 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate

*: Butyl Acetate

Fig.IV-37 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF B.A.*(40 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD + Sodium Sulfonate * Sorbitan Monooleate
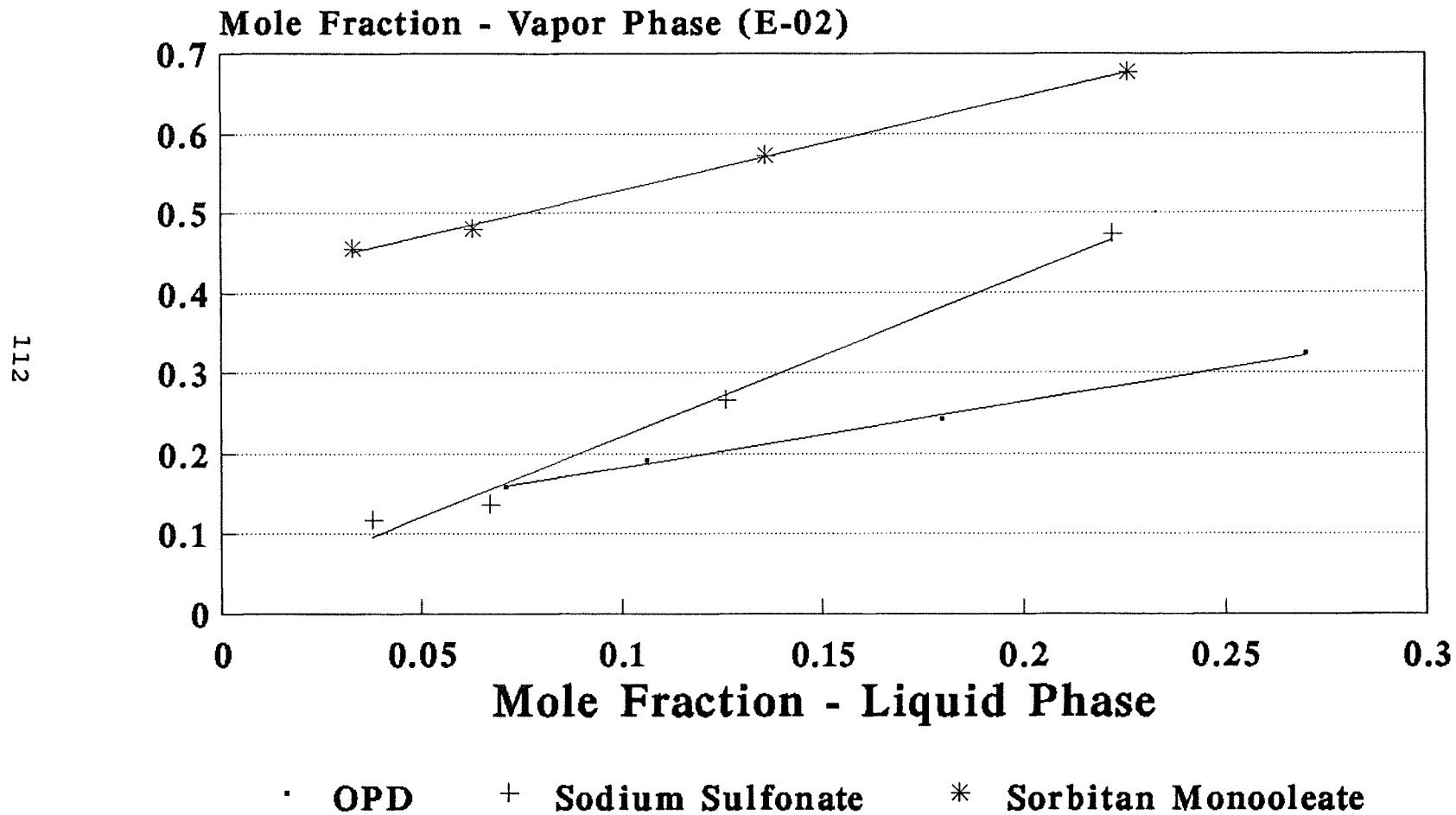
*: Butyl Acetate

Fig.IV-38 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF B.A.*(60 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate

*: Butyl Acetate

Fig.IV-39 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF B.A.*(70 C)
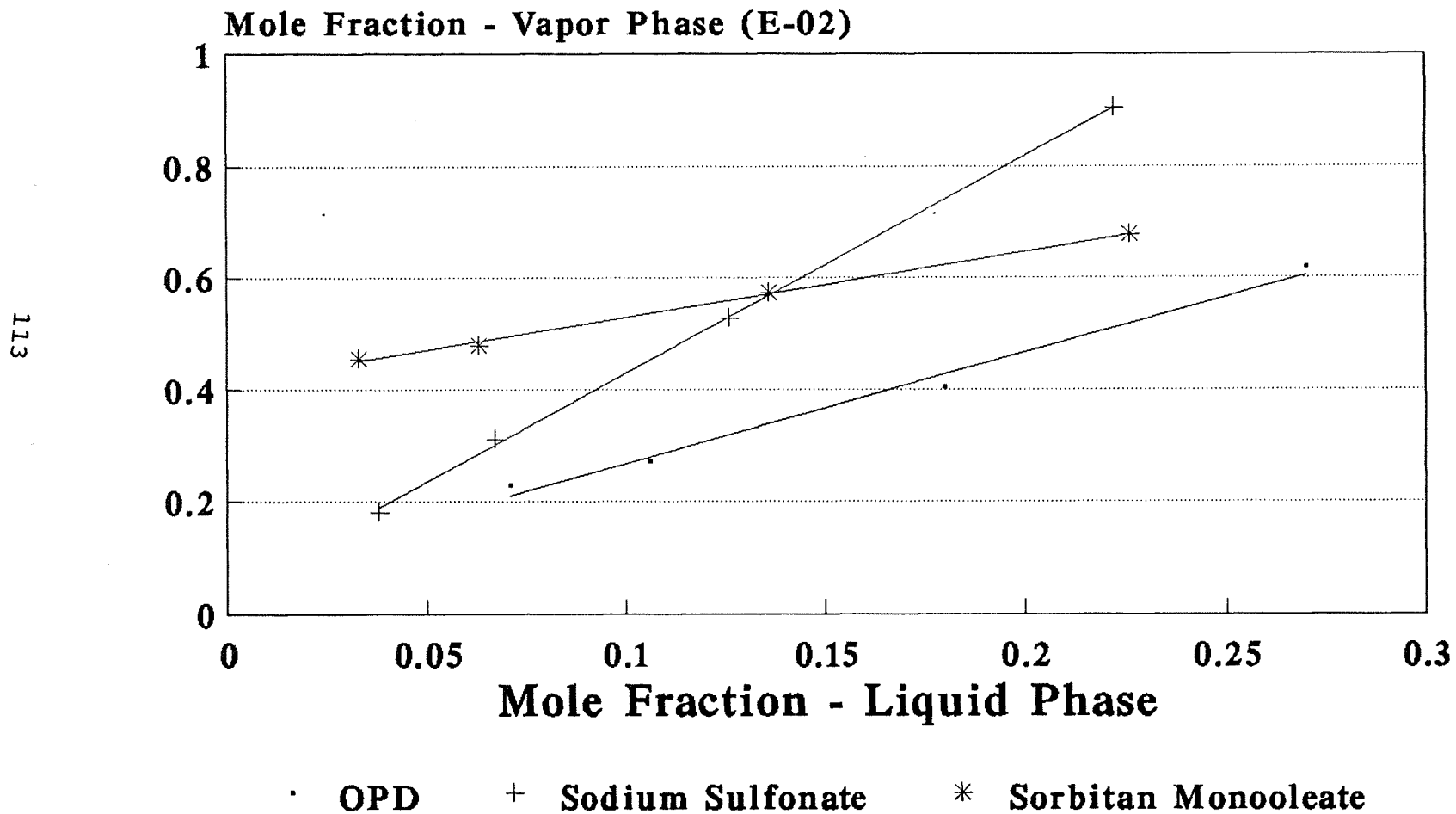

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate
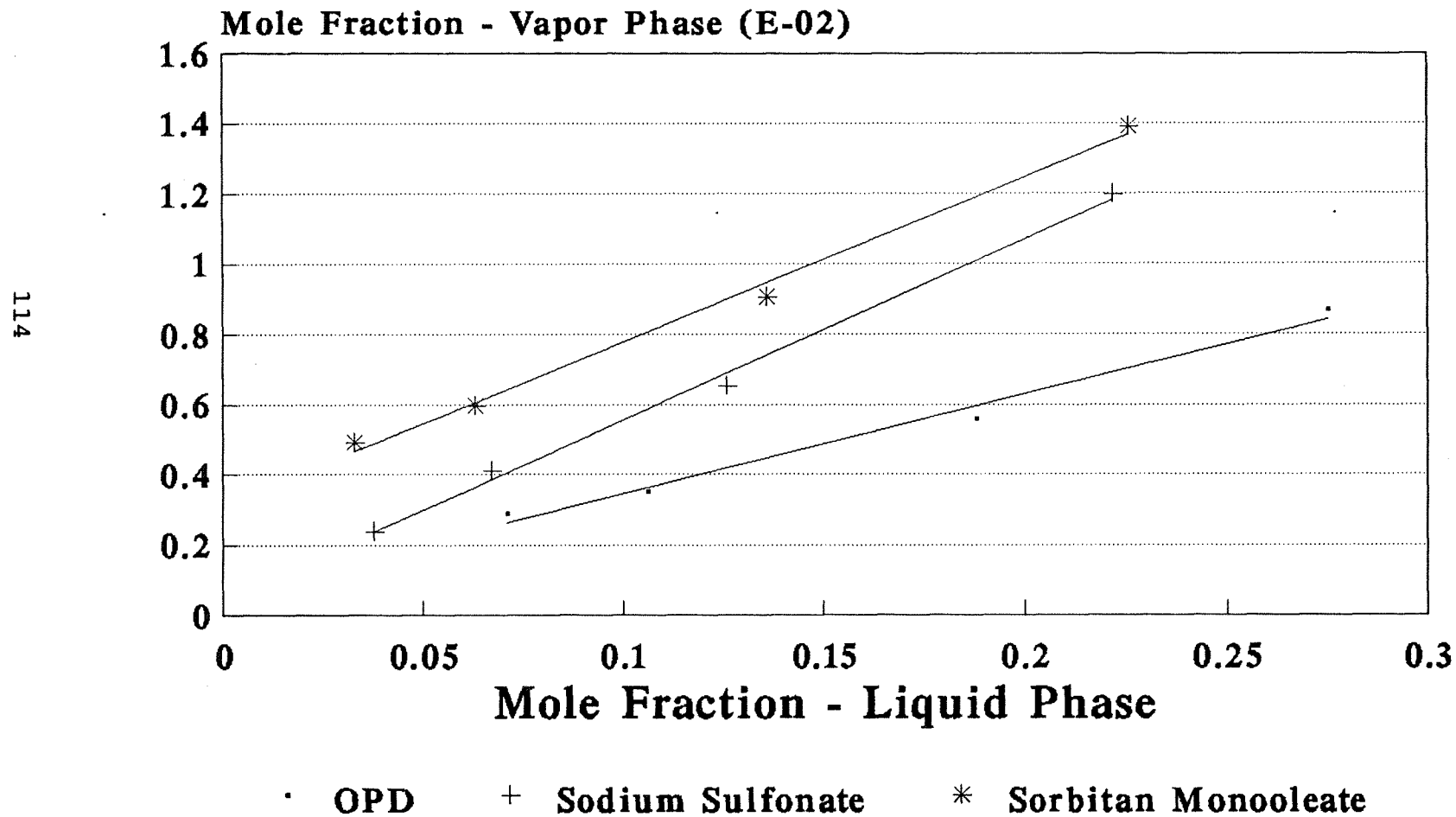
*: Butyl Acetate

Fig.IV-40 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF ACETONE (22 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

- OPD   + Sodium Sulfonate   * Sorbitan Monooleate

Fig.IV-41 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF ACETONE (40 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate

Fig.IV-42 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF ACETONE (60 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

- OPD   + Sodium Sulfonate   * Sorbitan Monooleate

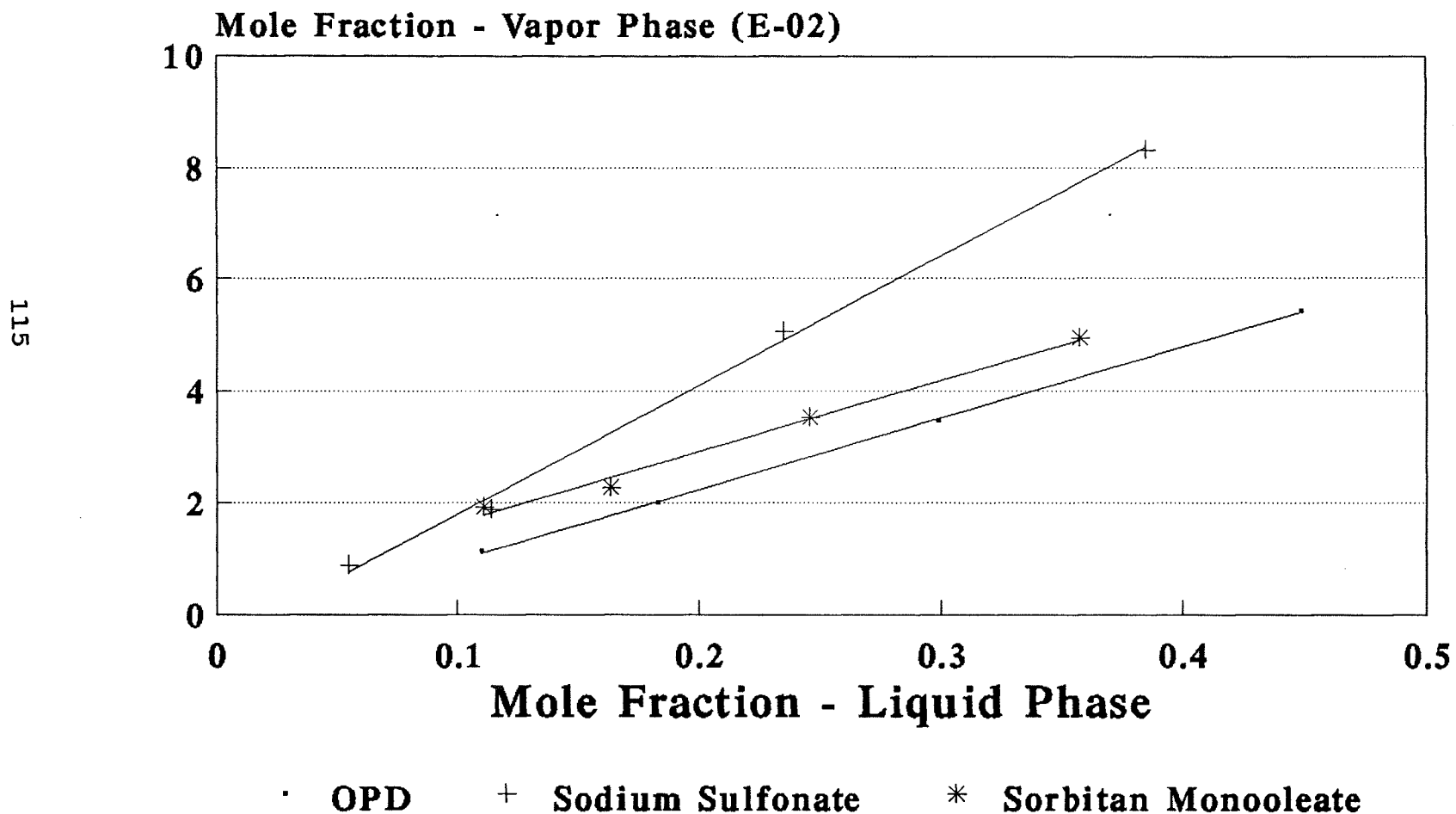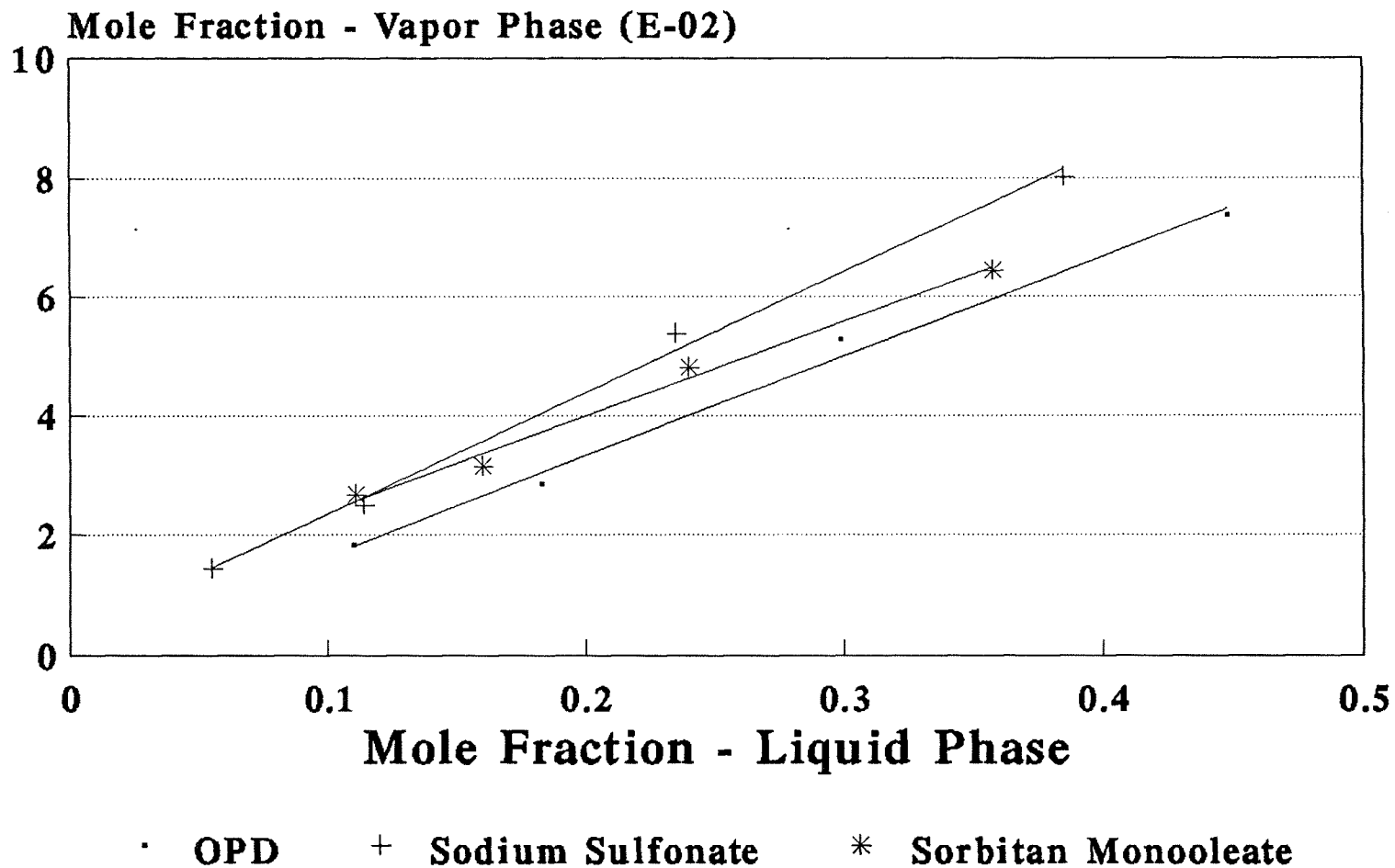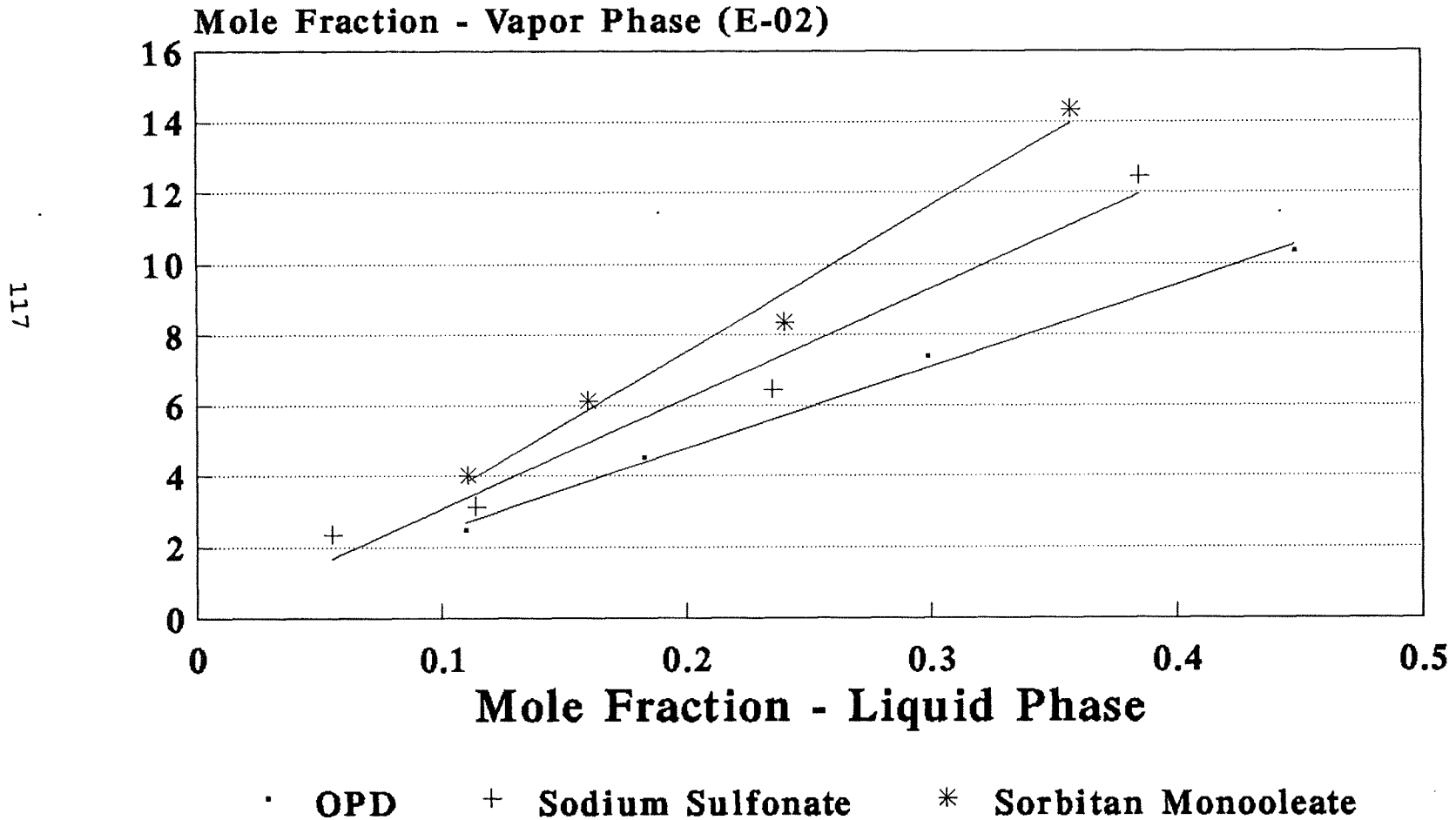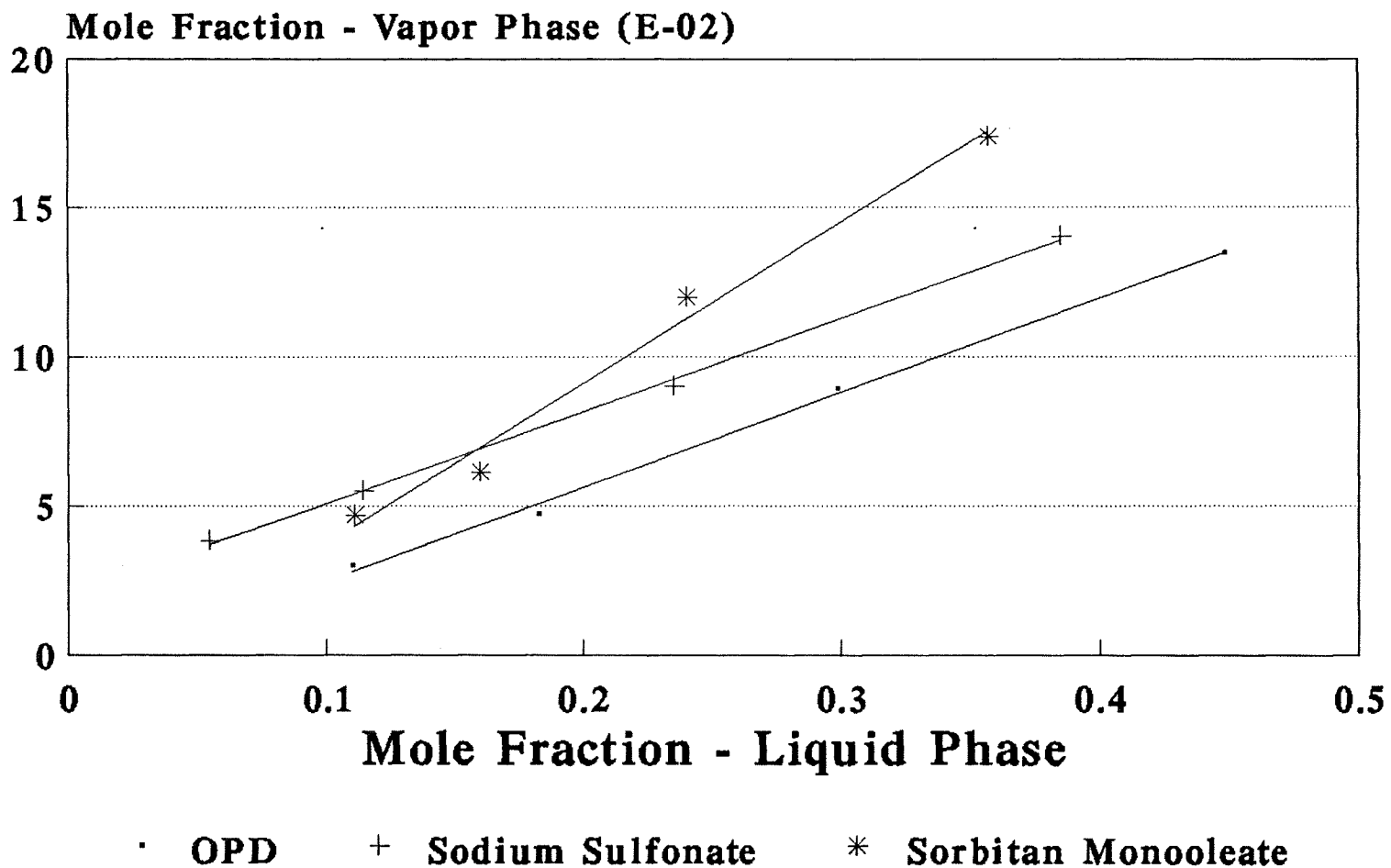# Fig.IV-43 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF ACETONE (70 C)

Fig.IV-44 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF i-PROPANOL (22 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate
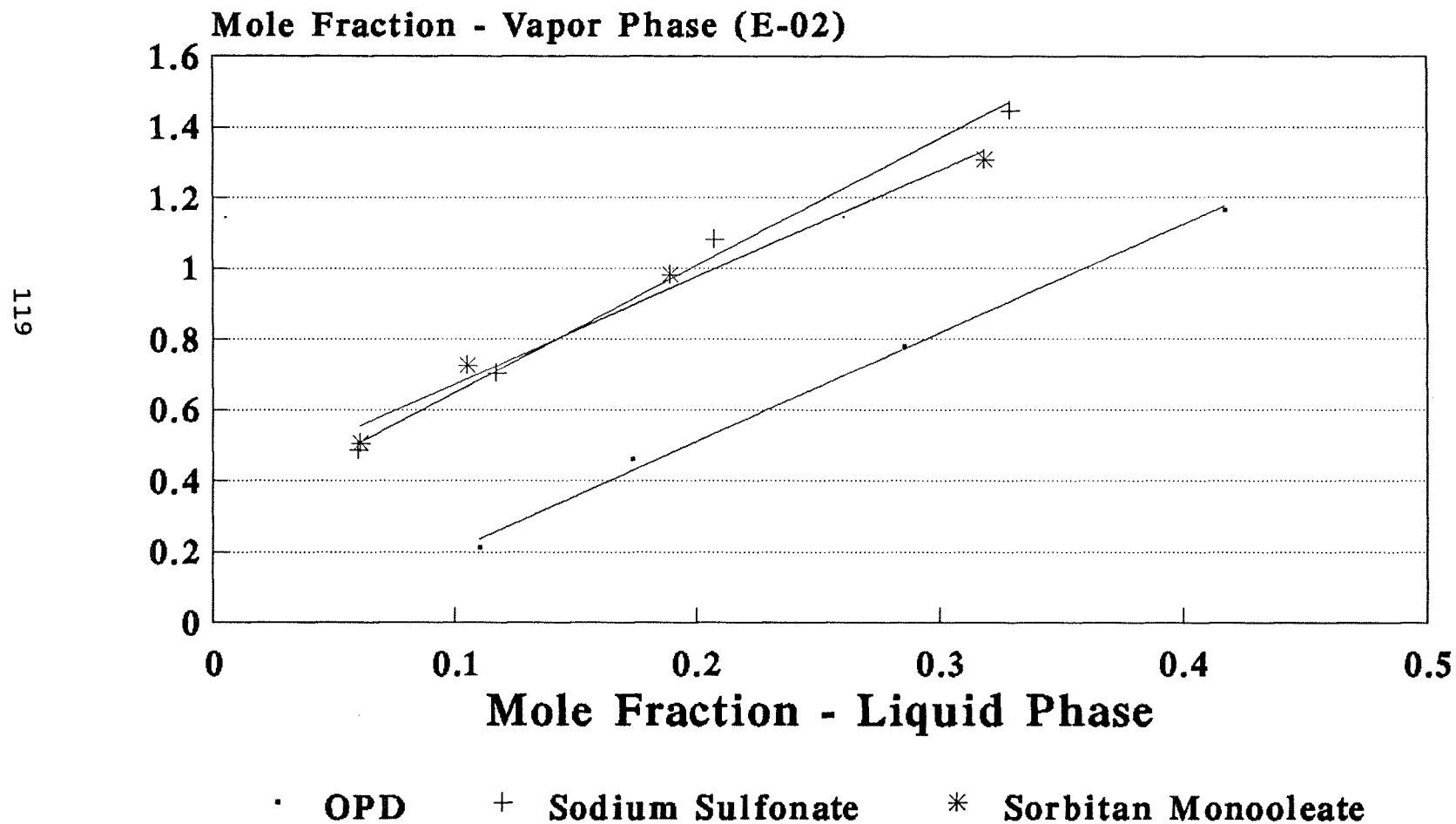
Fig.IV-45 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF i-PROPANOL (40 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate
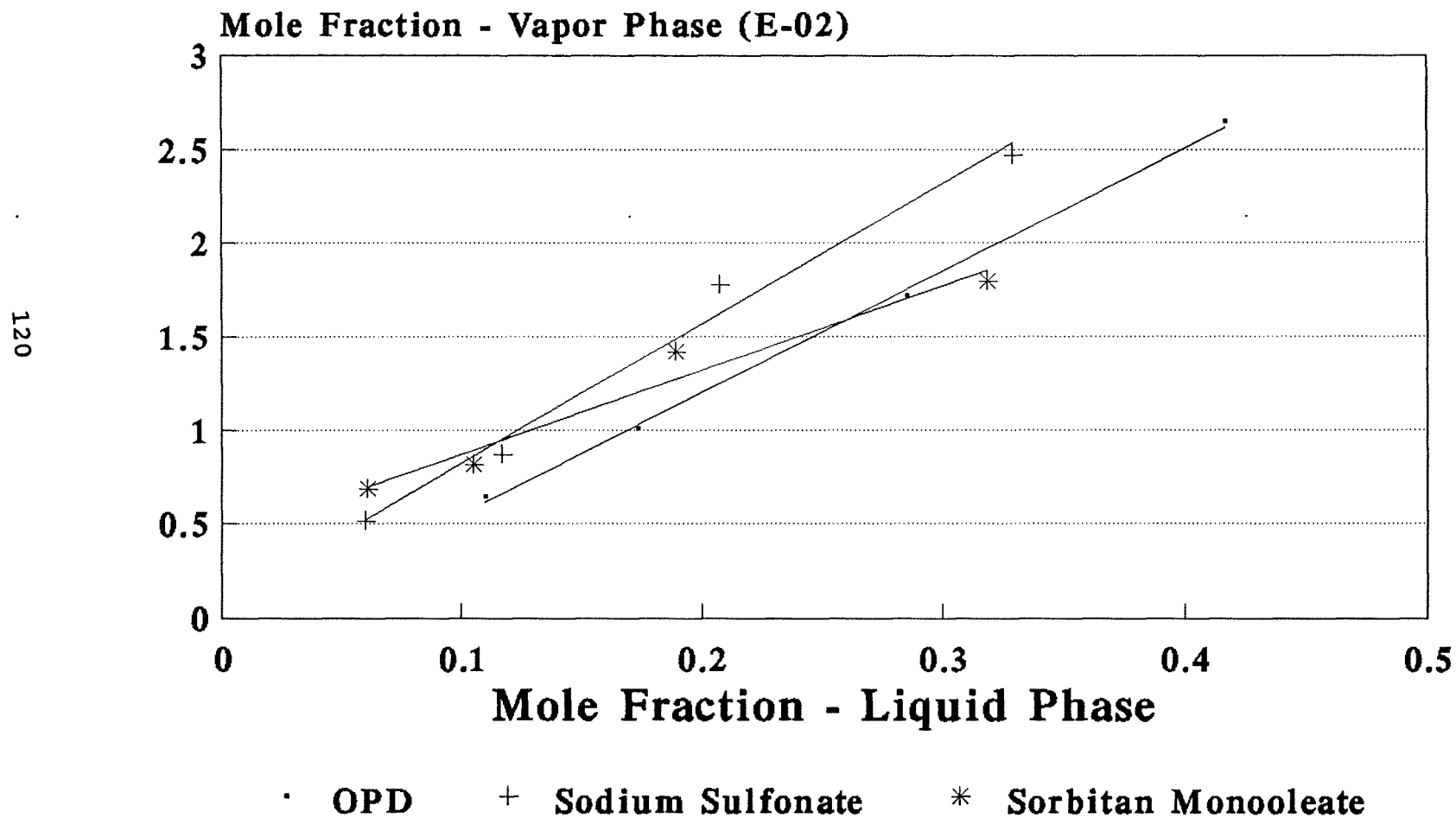
Fig.IV-46 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF i-PROPANOL (60 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate

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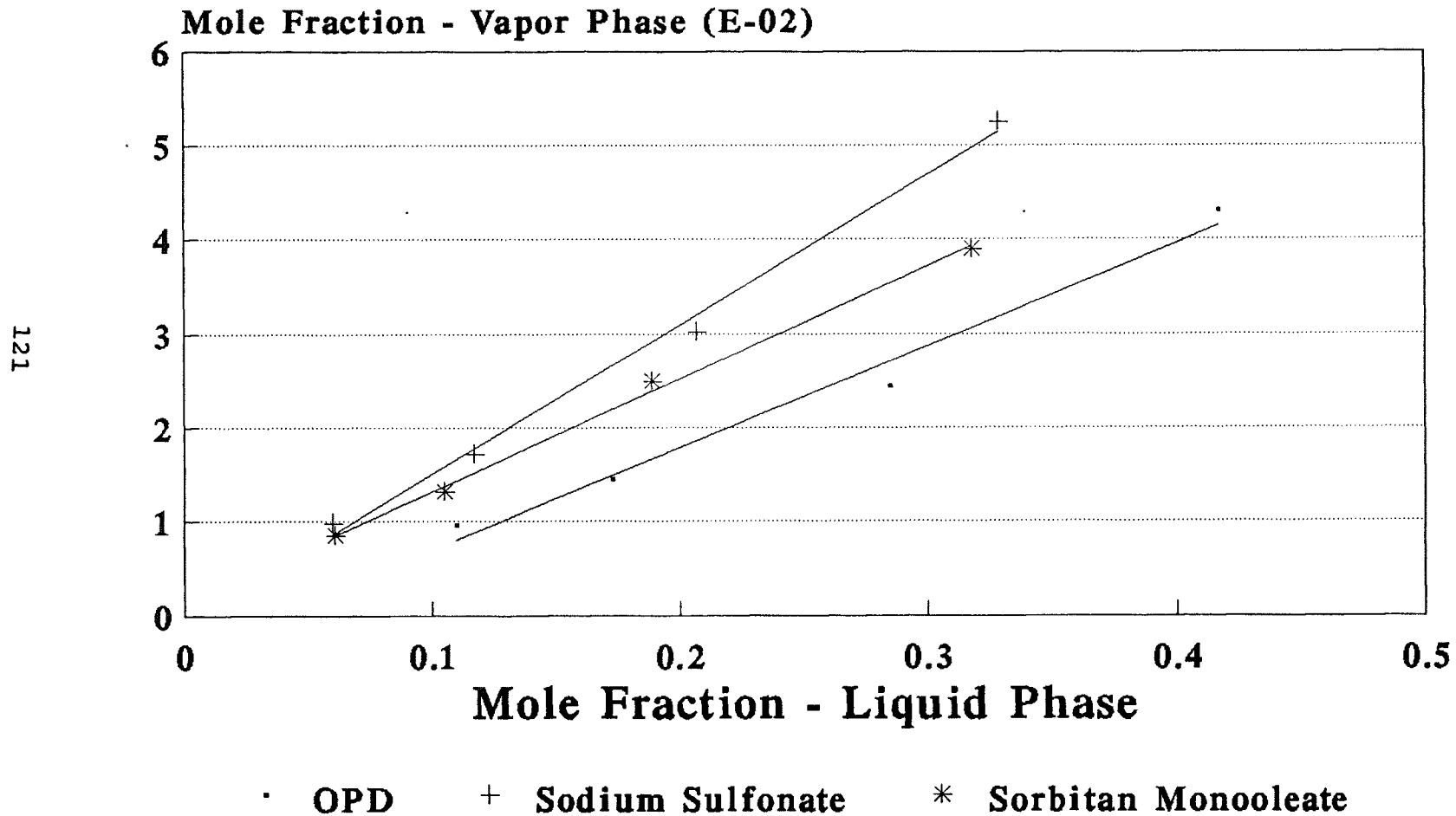
Fig.IV-47 EFFECT OF SURFACTANT ON VAPOR-LIQUID EQUILIBRIUM OF i-PROPANOL (70 C)

Mole Fraction - Vapor Phase (E-02)

Mole Fraction - Liquid Phase

· OPD   + Sodium Sulfonate   * Sorbitan Monooleate
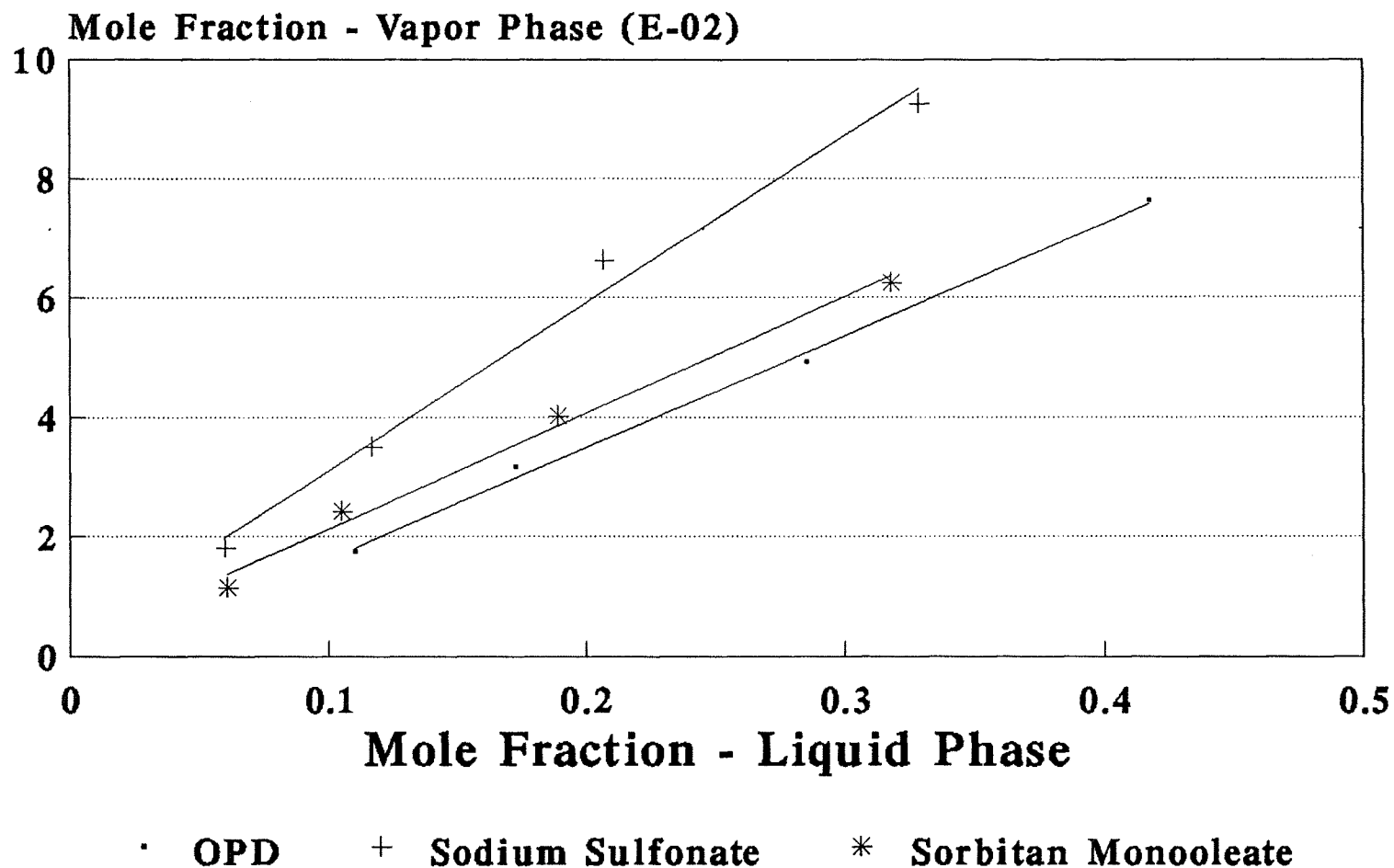
V. CONCLUSION

The vapor-liquid equilibria of five organics in each of three surfactants has been determined over a temperature range of 22 to 70 C. We can use this data to predict the degree of purification which can be achieved in removal of organics from air emissions given sufficient contact time to achieve equilibrium. The experimental results clearly demonstrate that the surfactants can absorb immiscible and partly immiscible organics from an air emission stream. The removal extent depends upon the surfactant type, specific organic solvents and the vapor-liquid equilibrium temperature. The solubility of these organics in surfactant is high enough to demonstrate capability of this method for use in purification of air emissions. However it is also evident that for each particular organic, a specific surfactant, organic concentration in air stream and operation temperature is necessary to obtain optimum results.

The experimental results indicate that for each target organic solvent, the mole fraction in vapor state is a linear function of its molar concentration in pure solvent . High solubility of each organic --- Toluene, Butyl Acetate, i-Propanol and MEK can be achieved by using Octylphenyl Decaethoxylate, Sorbitan Monooleate and Sodium Sulfonate to absorb. The surfactants are not, however, useful with all the organics we tested. Acetone does not show high absorption for example in these surfactants.

The results indicate distinctly that the mole fraction of organics in vapor phase increase linearly with the increase of the temperature.

For all organic compound-surfactant systems the solubilities increase as the mole fraction of organic solvent in surfactant liquid decreases.

Temperature directly effects the partial pressure of organic compounds. From Henry's law' the solubility of gas in liquid is function as its partial pressure, Thereby function as the vapor-liquid equilibrium temperature.

The three surfactants studied in this experiment show limited absorption of Acetone when liquid mole fraction of 0.05 to 0.45 at 22 C. Toluene and Butyl Acetate, are absorbed significantly by the surfactants when liquid phase mole fractions ranged from 0.05 to 0.35 at 22 C. Toluene is absorbed to the highest degree in all three surfactants. All the organic compounds show their lowest mole fraction in vapor state in Octylphenyl Decaethoxylate at all temperatures. Octylphenyl Decaethoxylate is shown to be the most efficient surfactant for elimination of these organic compounds from air emission.

The experiments justify further examination of surfactant scrubbing under actual operating conditions, such as a wet scrubber.

REFERENCES

1. D. H. Michael Bowen, "Solvent Vapors under Fire", Environment-
   al Science & Technology, Vol.5 No.11 1086-1088 (1971).

2. H. E. Garrett, "Surface Active Chemicals", 21-26, (1972).
   Pergamon Press Ltd., Jeadington Hill Hall, Oxford.

3. M. M. Dubinin "The Potential Theory of Adsorption of Gases
   and Vapors for Adsorbents with Energetically Nonuniform
   Surfaces", Chem. Rev. Vol. 60 235 (1960)

4. I. Atay, " Surfactant Enhanced Scrubbing of Hydrocarbon Vapors
   from Air Exhaust Streams in an Ejector Venturi Scrubber", 6-7,
   (1980). Master Thesis, NJIT.

5. A. Golovry and J. Braslaw, "Adsorption of Automotive Paint
   Solvents on Activated Carbon", Journal of the Air Pollution
   Control Association, Vol. 31, No. 8, (1981), 861-865.

6. W. J. Fisk, R. K. Spencer and D. T. Grimsrud, "Indoor Air
   Quality Control Techniques", 128-131, (1987). Noyes Data
   Corporation, Park Ridge, New Jersey.

7. K. C. Schifftner and H. E. Hesketh, "Wet Scrubbers", 1-3,
   (1986). Lewis Publishers Inc., Chelsea, Michigan.

8. P. V. Danckverts, F. R. S., "Gas-Liquid Reaction", McGraw
   Hill, Inc., New York, (1970), 17-20, 30-33.

9. C. McAuliffe, "Solubility in Water of Paraffin, and Cycloparaffin, Olefin, Acetylene, Cycloolefin and Aromatic Hydrocarbons", The Journal of Physical Chemistry, Vol. 70, No. 4, April (1966), 1267-1275.

10. D. F. Othmer and E. G. Scheibel, Trans. Am. Inst. chem., Engr., 37, 211-236, (1941).

11. W. K. Lewis and W. G. Whitman, "Principles of Gas Absorption.", Industrial Engineering Chemistry, 16, 1215-1220, (1924).

12. W. G. Whitman, Chemical and Metallurgical Engineering, 29, 147, 1923.

13. S. W. Benson, "Thermochemical Kinetics", 223, (1976). John Wiley & Sons, Inc., New York.

14. R. L. Duprey, "Compilation of Air Pollutant Emission Factors. National Center for Air Pollution Control. 67, (1968). Durham, N. C. PHS Publication Number 999-AP-42.

15. "Controlling Pollution from the Manufacturing and Coating of Metal Products." U. S. EPA Environmental Research Information Center, Technology Transfer, EPA -625/3-77-009, May 1977 Vol. 2, 34,.

16. U. S. Environmental Protection Agency, "Control of Volatile Organic Emissions from Existing Stationary Sources", Vol. 1 Research Triangle Park, N. CC. EPA-450/2-76-028, November 1979, 17-79,.

17. "Compilation of Air Pollution Emission Factors", 2nd Edition, U. S. Environmental Protection Agency, Research Triangle

N. C., February 1976.

18. C. L. Cutting and D. C. Jones, J. Chem. Soc., 4067-4075, (1955).

19. D. Mirev, D. Elenkov and Khr. Balarev, Isv. Inst. Obsheha Neorg. Khim., Org. Khim., Bulgar Akad. Nauk, 8, 73-81, (1961).

20. M. J. Rosen, "Surfactants in Emerging Technologies", 169-186, (1987).

21. M. J. Rosen, "Surfactants in Emerging Technologies", 187-205, (1987).

22. M. J. Rosen, "Surfactants in Emerging Technologies", 151-187, (1987).

23. M. J. Rosen, "Surfactants and Interfacial Phenomena", 2-3, (1978). John Wiley & Sons., New York.

24. A. C. Morresi " Soluble Surfactant Effects On Gas Absorption Of Organic Compounds", 22-23, (1975). Master Thesis, NJIT.

25. M. J. Rosen, "Surfactants and Interfacial Phenomena", 56, (1978). John Wiley & Sons., New York.

26. B. Thompson, "Fundamentals of Gas Analysis by Gas Chromatography", 95-114, (1977). Academic Press Inc., New York.

27. P. B. Gove Ph.D. "Webster's Third New Intrnational Dictionary", G & C Merriam Co. Publisher , Massachussetts.

28. R. C. Weast Ph.D. and M. J. Astle Ph.D. "Handbook of Chemistry and Physics" 63 rd Edition 1987-1988, CRC Press, Inc,. Boca Raton. Florida.

29. W. M. Linfield, "Anionic Surfactants" Part II, Marcel Dekker Inc., New York (1976).

30. T. K. Sherwood, "Absorption and Extraction", 2nd Edition, McGran-Hill Book Co., New York.