THE SOLUBILITY OF HEXACOSANE

IN

2 ETHYL N BUTYRIC ACID, PROPIONIC ACID,

AND

ACETIC ACID

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Alan N. Mearns

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ABSTRACT

The solubility of a long chain paraffin hydrocarbon ($C_{26}H_{58}$) over a temperature range of $75°$ has been measured in acetic, propionic and ethyl butyric acids. The phase relationship for the acetic acid - hexacosane system differs considerably from that of the other two. The results show that propionic acid is the best solvent to use for recrystallization and purification of a long chain hydrocarbon.

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Introduction

During the last ten years several researches have been undertaken at the University of British Columbia on the mutual solubilities of hydrocarbons. This work together with information supplied by other universities has helped establish the fact that the mutual solubility of hydrocarbons is a function of their molecular weights. Use has been made of this knowledge by the petroleum industry to isolate and purify petroleum fractions by pointing out the most suitable solvent to be used and indicating the range in which any specific solvent would be applicable.

Most information on solubilities has been of a qualitative nature. As a result, there is much need for quantitative data which, when applied to existing theoretical equations, may add support to, or help disprove, existing conceptions of the laws governing solubility.

The need of the petroleum industry for such information has arisen from the increased use of solvent extraction

processes in supplementing older refining methods. Increased speeds, pressures, and temperatures in automotive and aviation engines have demanded more stable lubricants, and hence more efficient refining methods to obtain these lubricants. Examples of these solvent extraction processes are to be found in various patent records.

This present research was undertaken to provide fundamental data on the solubility of the hydrocarbon hexacosane, $C_{26}H_{54}$, in three organic acids -- 2 ethyl n butyric acid, propionic acid, and acetic acid. It is hoped that this data may prove to be of some use in solvent extraction work.

Theory of Solubility

Solid-Liquid Systems

Equilibrium between solid and liquid in a two component system may be considered from two points of view. If the liquid mixture is in equilibrium with the solid phase in excess, the solution is said to be at its freezing point, and the curve representing the variation of this temperature with the composition of the system is known as the freezing point curve. If, on the other hand, a relatively small proportion of solid phase is in equilibrium with the liquid, the system is said to be a saturated solution and the variation of temperature with composition is represented by a solubility curve. There is no fundamental difference between freezing point curves and solubility curves. Common practice is to refer to freezing point curves when dealing with a system in which the two components are chemically similar, e.g., when both are

metals, salts, or organic compounds of not very different melting point. When the two compounds are chemically different or there is a marked difference in their melting points, it is possible to make the conventional distinction between solvent and solute. In such a case, the condition under which the solid solute separates out is indicated by a solubility curve, while the equilibrium between the liquid and solid solvent is represented by a freezing point curve. More conveniently, the whole curve may be referred to as a solubility curve.

Calculation of Freezing Points and Solubilities

By use of the Clausius-Clapeyron equation, Glasstone[1] derives the following general form of Hildebrande's equation[2]:

$$\ln x = - L_f/R(1/T - 1/T_0)$$

for constant pressure conditions, where T is the temperature at which the solid present to the extent of x mol fraction in the mixture is in equilibrium with the liquid. L_f is the heat of fusion of the solid and T_0 is its melting point in the pure state. The derivation of this equation involves no assumption concerning the nature of the solid phase, and so it applies equally to both components of the liquid mixture. In the general form given above, it is assumed the mixture behaves ideally. It is thus possible, by means of this equation, to calculate the freezing point T of a solution in which x is the mol fraction of the solvent; alternately, the equation gives the solubility, i.e. mol fraction x, at the temperature T. In each case L_f and T_0 refer to the component separating as the solid phase. This equation is limited in its usefulness

by scarcity of data on latent heats of fusion. Also, deviations are observed because the systems do not behave ideally.

By observation of the above equation several qualitative deductions of interest may be made. It is seen that for substances having similar molar heats of fusion, those with lower melting points have the higher solubilities. Since T must always be less than the melting point T_0, it follows that solubility must increase with temperature: further, the heat of solution must be equal to the heat of fusion of the solute, provided the system behaves ideally.

Condensed Systems

Since three degrees of freedom - temperature, pressure, and composition - are possible in a two component system, a three dimensional figure would be required to represent accurately the conditions of equilibrium of such a system. This representation may be simplified considerably by arbitrarily fixing one of the variables. In solid-liquid systems the effect of pressure is relatively small, and measurementsmade under atmospheric pressure would be very little different from those obtained if the solid and liquid are in equilibrium under their own vapor pressure. A system in which only solid and liquid phases are considered is called a condensed system. Such a system may be graphically represented by the use of only two variables - temperature and composition. Such a manner of representation was emplyed in this research.

Liquid-Liquid Systems

In the study of the mutual solubilities of liquids it is generally the practice to work, not at the vapor pressure

of the system, but at atmospheric pressure, and to determine

the compositions of the two layers at various temperatures.

For a system of two components in which there are two liquid

phases in equilibrium the phase rule shows that there are two

degrees of freedom, so if the pressure is fixed at one atmo-

sphere, the temperature is sufficient to define the system

completely. In other words, at a given temperature the comp-

ositions of the two liquid layers are fixed and are independent

of the amounts of the two phases.

By making use of the Alexejeff or synthetic method,

as was done in this research, and studying the whole range of

mixtures, a complete solubility curve may be obtained. If the

compositions of the conjugate solutions at each temperature

are plotted, most systems give a curve similar to that shown

in the following figure:
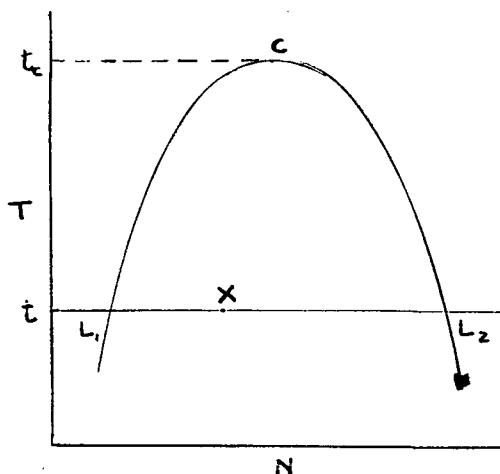
At any temperature t, the conjugate solutions have compositions

as indicated by the points L_1 and L_2. The synthetic method

gives only one of the two points representing the composition

and temperature at which the second layer is negligable in

amount. This point is in effect the composition of one of the two layers. By covering the whole range of concentrations the complete solubility curve may, however, be obtained. The tie lines joining the two points representing two layers in equilibrium at a given temperature are, of course, horizontal.

It may be seen from the figure that, as the temperature is raised, the compositions of the two layers approach each other until eventually point C is reached at temperature t_c when the two layers become one; t_c is known as the "critical solution temperature" or "consolute temperature". Above this temperature the two liquids are miscible in all proportions. In fact, all systems lying outside of the curve consist of one layer only, while those lying inside the curve consist of two layers, the compositions of which are given by points on the curve for the same temperature. For example, a system designated by point X will consist of two layers L_1 and L_2, the relative amounts being given by:

$$\frac{\text{Amount of } L_1}{\text{Amount of } L_2} = \frac{\text{Distance } XL_2}{\text{Distance } XL_1}$$

Materials Used

The hexacosane used in this research was synthesized by the Peterson electrolytic method from Eastman Kodak myristic acid[3]. It was purified by treatment with small quantities of concentrated sulfuric acid following the method of Piper et al[4] and further purified by repeated crystallization from benzene until a constant melting point of 55.6°C was obtained.

In the literature, various values for the melting point of hexacosane are to be found. Four of these are listed

in chronological order:

$$56.4[5], \; 57[6], \; 56.1[7], \; 55.8[8].$$

Garner, van Bibber, and King give the following equation for the melting point of hydrocarbons:

$$T = (0.6085n - 1.75)/(0.001491n \; / \; 0.00404)$$

where T is the absolute temperature and n is the number of carbon atoms in the hydrocarbon. Using this equation, the melting point of hexacosane is calculated to be 55.6°C. The melting point of the hexacosane used in this research is thus seen to be in exact agreement with the calculated value and in very close agreement with latest observed values.

The 2 ethyl n butyric acid was purified in the laboratory by recrystallization andhad a boiling point of 190° C. A technical grade of Eastman Kodak propionic acid with a boiling point of 141.1°C, and Baker's Analyzed C.P. glacial acetic acid with a boiling point of 118.1°C was used.

Experimental Procedure

Alexejeff's synthetic method for the determination of solubility was decided on as being the most practical method of obtaining the desired results. This method consists of preparing a mixture of carefully determined amounts of solute and solvent in a sealed bulb to prevent vaporization, and then gradually raising the temperature until the last crystal of solid disappears, at which point the temperature is noted. On recooling the bulb and its contained liquid a point is reached at which the solid begins to crystallize out. The mean of these two points represents the solubility of one compound in the other. The mean is taken in order to counter-

act the effects of temperature lag and supercooling.

Thick walled bulbs of approximately 2 cm. in diameter were blown and sealed to stems of 6 mm. glass tubing, 15 cm. in length. The hexacosane was introduced into the bulb by melting and pouring through a long stemmed funnel. The solvents, which were all liquids at room temperature, were merely run through a long stemmed funnel into the bulb. Correct weights of solvent and solute were obtained by weighing the bulb before and after introducing both hexacosane and the solvent. The contents of the bulb were then frozen with dry ice in a Dewar flask and sealed to a vacuum line. By alternately evacuating the bulb and sweeping it out with hydrogen, most of the air in the bulb was thought to be removed and the bulb was then sealed. Thus the solid and liquid in the sealed bulbs were in equilibrium under their own vapor pressure.

The prepared bulbs were then placed in a water bath equipped with an electric immersion heater, cooling coils, and an electric variable speed stirrer. By alternately raising and lowering the temperature of the bath, and noting the points at which the last crystal of hexacosane disappeared and then reappeared, the critical point for each bulb was obtained. This system was used with good results to study the systems hexacosane- 2 ethyl n butyric acid and hexacosane-propionic acid.

When the system hexacosane-acetic acid was studied, it was found that the two components were not mutually soluble below the melting point of hexacosane except at very minute molar concentrations of hexacosane. Because of this fact, a

liquid-liquid system resulted and the temperature had to be raised considerably above the melting point of hexacosane before the point of mutual solubility was obtained. A paraffin bath was employed in order to reach the desired temperatures. The critical point was defined quite sharply by the disappearance of the two layers on raising the temperature and by a sudden turbidity on lowering the temperature. This point of turbidity was very sharp and reproducible and was considered to be the more accurate indication of the mutual solubility.

Because of the low vapor pressures of the liquids used, at the experimental temperatures, and the small volume of the bulbs above the liquid, corrections for vaporization of the solvent in the bulb were thought to be unnecessary and were not applied.

Results

Table 1.

Hexacosane - 2 Ethyl n Butyric Acid

Hexacosane, g.	Butyric Acid, g.	Mol % Hexacosane	F.P., °C
.....	.....	0.0	< -15
0.0200	2.5281	0.25	19.5
0.0834	1.9698	1.33	30.88
0.2633	1.4492	5.45	40.32
0.3279	1.1552	8.23	42.98
0.4348	0.7383	15.72	45.82
0.4164	0.6406	17.0	46.02
0.8276	0.7681	25.5	47.38
0.6305	0.5443	26.9	47.71
0.9602	0.5690	34.9	48.55
1.3078	0.4477	48.0	49.09
1.2273	0.1358	74.2	51.40
0.9958	0.0769	80.4	52.28
......	......	100.0	55.6

N.B. Temperatures tabulated in these tables are the means of a large number of readings. Although the readings were taken to the nearest hundredth of a degree, and hence the tabulated results are given to the nearest hundredth, it is felt that results are accurate only to the nearest tenth.

Table 2.

Hexacosane - Propionic Acid

Hexacosane, g.	Propionic Acid, g.	Mol % Hexacosane	F.P., °C
.....	.....	0.0	-22
0.0436	3.6116	0.24	30.68
0.0807	2.7604	0.59	37.31
0.2422	0.9891	4.72	43.85
0.4477	0.8019	10.1	46.75
0.5038	0.5992	14.5	47.08
0.6870	0.5329	20.65	47.36
1.0159	0.3694	35.7	48.65
1.4838	0.3248	48.0	48.85
1.5628	0.1196	72.6	50.45
1.8411	0.0774	82.8	51.82
.....	.....	100.0	55.6

Table 3.

Hexacosane - Acetic Acid

Hexacosane, g.	Acetic Acid, g.	Mol %Hexacosane	Miscibility Pt.
......	......	0.0	16.6
0.1491	1.4658	1.64	180.0
0.4660	0.8473	8.30	186
0.8806	0.4876	22.0	170
1.0788	0.3714	32.2	137
1.6603	0.3601	42.9	109.5
1.4019	0.1998	53.5	90
.....	.....	100.0	55.6
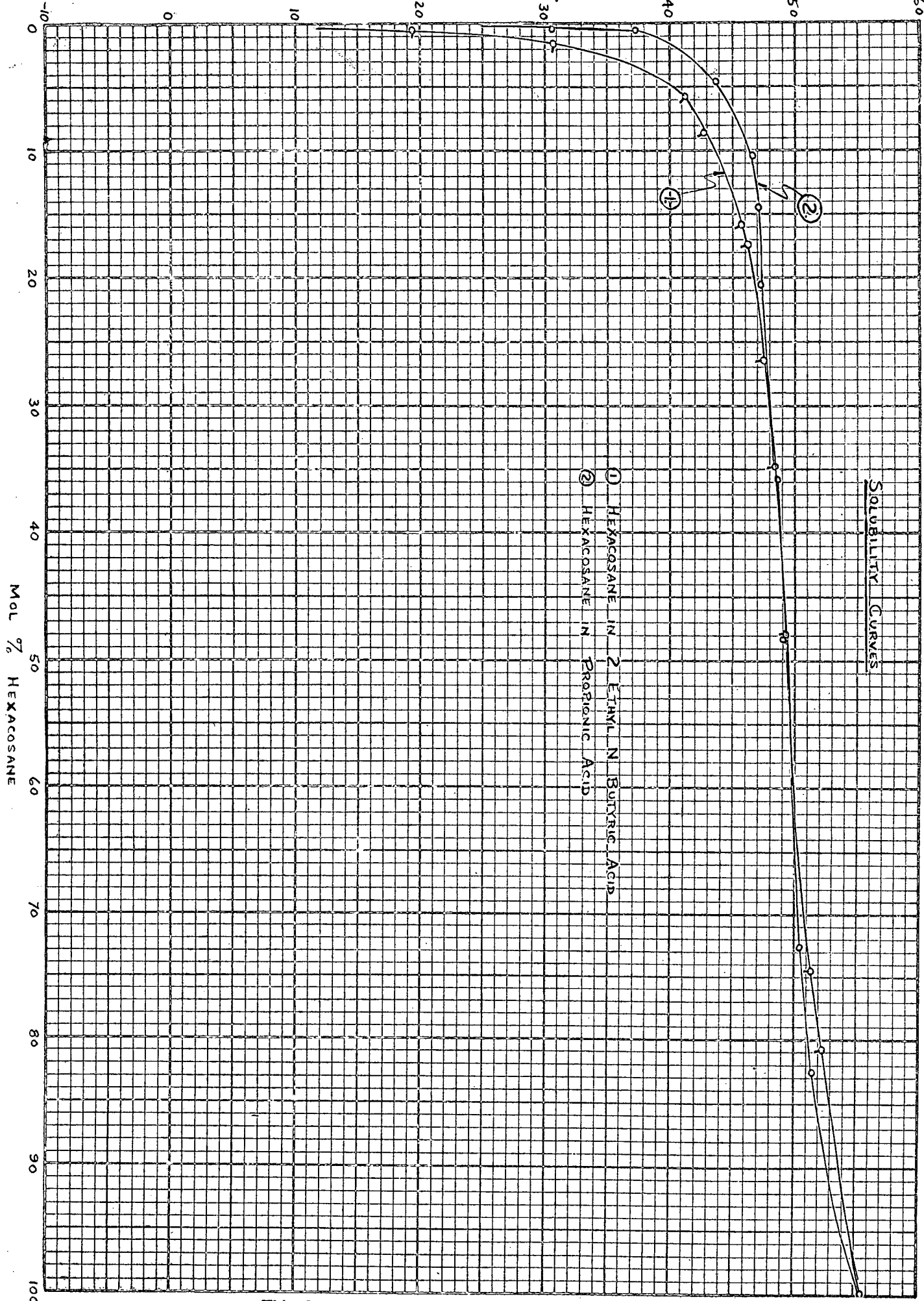
Fig. 1

SOLUBILITY CURVES

(1) HEXACOSANE IN 2 ETHYL N BUTYRIC ACID
(2) HEXACOSANE IN PROPIONIC ACID

TEMPERATURE, °C.

MOL % HEXACOSANE

This plate 10 x 7 inches. Edge of each small square 1/10 inch.

C.C.C.
T.

Temperature , °C

Mol % Hexacosane

Liquid-Liquid System

Solubility of Hexacosane in Acetic Acid

$$\ln x = -\frac{L}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

This plate 10 x 7 inches. Edge of each small square 1/10 inch.

C.C.C.
T.

$$\ln x = -\frac{L_f}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

① HEXACOSANE IN 2 ETHYL N BUTYRIC ACID

② HEXACOSANE IN PROPIONIC ACID

Log x (vertical axis)

$10^4/T$ (horizontal axis)

FIG. 3
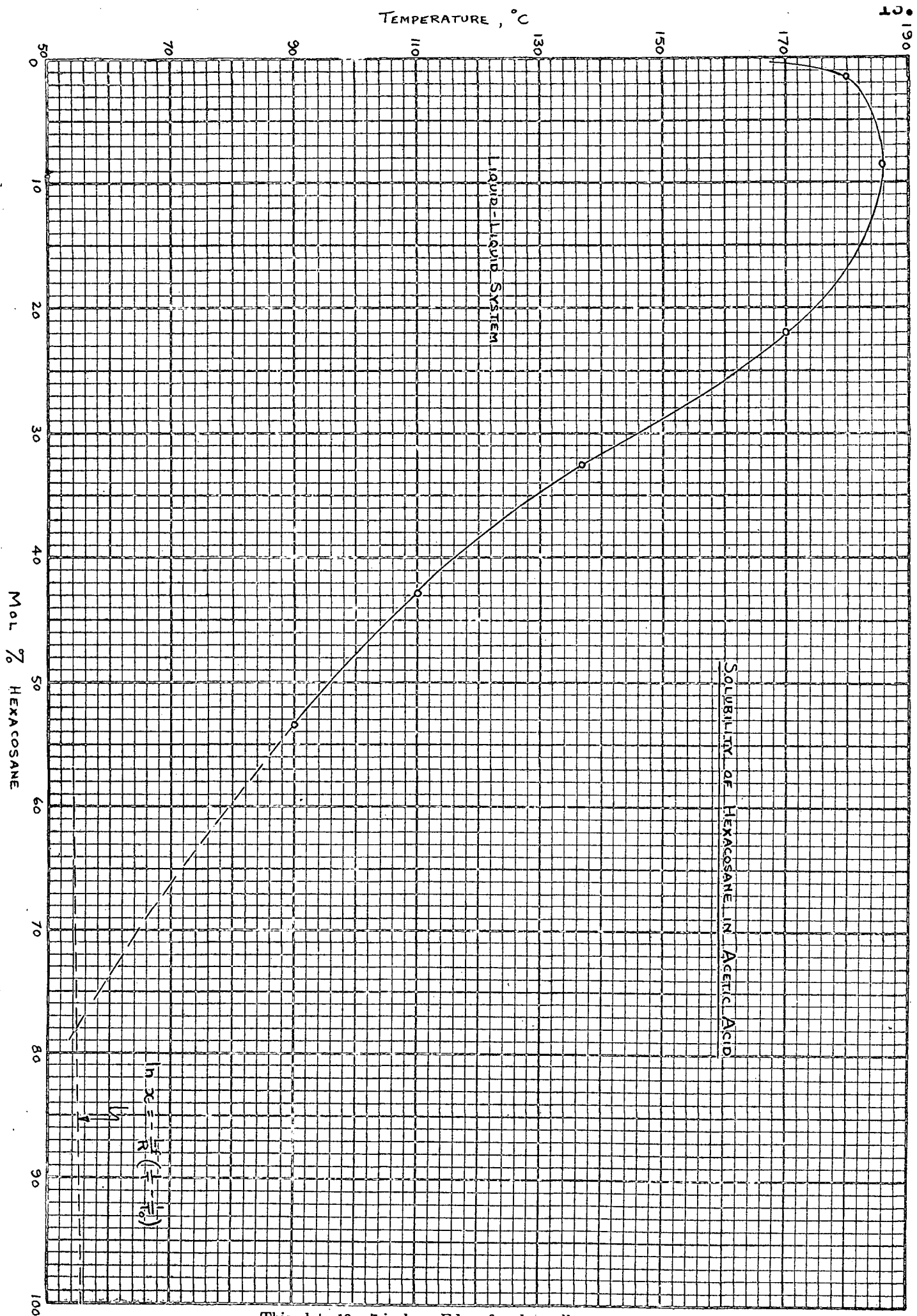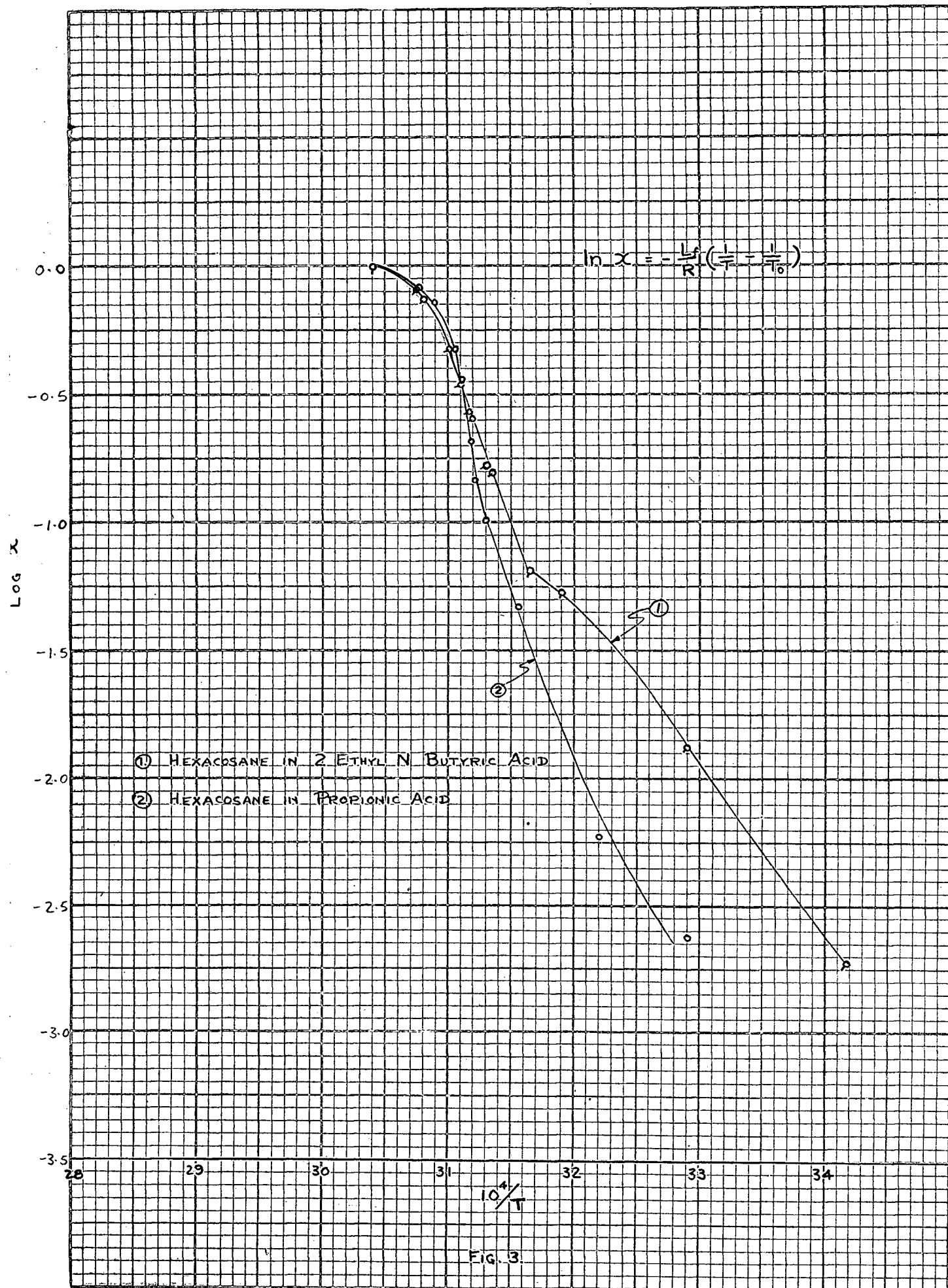
This plate 10 x 7 inches. Edge of each small square 1/10 inch.

C.C.C.
T.

Discussion of Results

By plotting mol concentrations against temperature
for the systems hexacosane - 2 ethyl n butyric acid and
hexacosane propionic acid the curves in fig. 1. were obtained.
Fig. 2. gives the curve obtained for the system hexacosane -
acetic acid, which was a liquid-liquid system. In fig. 3.,
log x vs. 1/T is plotted for the two solid-liquid systems of
fig. 1.

From an observation of figs. 1 and 3 it may be seen
that after a concentration of about 10 mol percent is reached
the solute would appear to exert its influence in determining
the shape of the curves. Also, when a temperature of about
$50^{\circ}C$ is reached, there is another change in the slope of the
curves. This is seen most strikingly in fig. 3. where a change
of slope denotes a change in the latent heat of fusion. This
temperature of $50^{\circ}C$ corresponds very closely to $50.1^{\circ}C$ as
reported by Garner et al.[7] to be the transition point for the
change from the α to β form of hexacosane. It would appear
obvious from the shape of the curves that the systems are not
ideal. Therefore L_f in the equation

$$\ln x = -L_f/R(1/T - 1/T_0)$$

should be replaced by the differential heat of solution. This
fact would help explain the changes in slope of the curves of
fig. 3. At low mol percentages of hexacosane the differential
heat of solution corresponds very closely to the heat of
dilution of the solvent. From about 10 mol percent up to the
transition point, the differential heat of solution corresponds

more closely to the latent heat of fusion of β hexacosane,
and the curve approaches the ideal, which is a straight line
with slope - L_f/R. After the transition point is reached, we
are dealing with the α form of hexacosane and the slope of
the curve again changes, approaching the latent heat of fusion
of α hexacosane. The discontinuity seen in the curve for
hexacosane - 2 ethyl n butyric acid is perhaps due to association
of the acid with the hexacosane. This system does not appear
to act normally.

In fig. 2. the solubility curve for hexacosane in
acetic acid is plotted accurately up to about 54 mol percent
hexacosane. For increased concentrations of hexacosane the
surface area between the two liquids was so small, and the
point of turbidity so indistinct, that accurate results could
not be obtained by visual methods. We know from crystallization
work that the melting point of hexacosane is slightly depressed
in the presence of acetic acid. This is indicated in fig. 3.
by the dotted curve plotted from Hildebrande's equation. From
the data given, it is seen that the critical solution temperature
of the system hexacosane - acetic acid is 187^0C.

Purification by Recrystallization

In order for a solvent to be a satisfactory
recrystallizing medium, to be used in purifying a desired
product, it is necessary that the solubility curve have a small
temperature gradient in the desired range. That is to say, for
a small decrease in temperature a comparatively large amount of
solute must separate out. It would appear from this research

that decreasing molecular weight increases the recrystallizing effect of organic acids in purifying paraffins. For hexacosane, propionic acid is seen to be the best recrystallizing medium, inasmuch as it gives the largest amount of the paraffin separating out for a given decrease in temperature. Recrystallization is most effective between 10 and 60 mol percent of hexacosane. In the system hexacosane-acetic acid, the fact that a liquid-liquid system is obtained makes the acid unsuitable for recrystallization.

Conclusions and Recommendations

In future solubility studies of this type, the author feels that certain refinements in technique would make the work more accurate and less tedious. In the visual method as employed in this research, each bulb required undivided attention during the period of raising and lowering the temperature, which was usually a long, drawn out operation. The temperatures reported are the means of a large number of observations for each bulb. It is felt that the critical point could be obtained more quickly and more accurately if a strong beam of light were directed through the solution in the bulbs to detect the crystals of solute by reflection, immediately on precipitation. Some method of preventing supercooling would also prove very effective, as constant agitation appears to have very little effect. This might possibly be done by sealing a piece of inert wire in the bulb, and touching the external end of the wire with dry ice when approaching the critical point from above. This would afford a center of precipitation for the

crystals of solute and would decrease supercooling to a minimum.

Summary

1.   The solubility curves for the systems hexacosane - 2 ethyl n butyric acid, hexacosane - propionic acid, and hexacosane - acetic acid have been found.

2.   The critical solution temperature of the system hexacosane-acetic acid is seen to be 187°C.

3.   The data obtained adds support to the belief that hexacosane exists in two enaniotropic forms. The trasition temperature would appear to be about 50°C.

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