VISCOSITY AND ULTRASONIC VELOCITY IN NONASSOCIATED HYDROCARBON LIQUID MIXTURES

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PREFACE

The primary objective of this research project was to serve as a pilot project for a series of research projects aimed at a better understanding of the liquid state. The development of a correlation between viscosity and ultrasonic velocity in nonassociated hydrocarbon liquid mixtures was a direct outcome of this work. Also of interest was a correlation between ultrasonic velocity and density in nonassociated hydrocarbon liquid mixtures. In the course of this work, density, viscosity and ultrasonic velocity data were taken on 47 binary, ternary, and quaternary mixtures and on the five hydrocarbons from which they were made. The results are promising and point to many interesting research projects for future workers.

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CHAPTER I

INTRODUCTION

Motivation for This Work

When chemical engineers are engaged in designing and operating industrial plants, they must deal with many types of fluids. Among the various pieces of information that they must have in their work are the physical properties of these fluids. Because of the wide variety of fluids and the broad ranges of temperature, pressure, and composition encountered, experimental data are usually either inadequate or do not exist at all. In addition, because of time and economic limitations or physical unavailability, it is nearly always inconvenient to draw a sample of the fluid and measure its physical properties. Therefore, much effort has been expended by engineers and scientists in trying to estimate these physical properties a priori.

It was with these facts in mind that this research project was undertaken. The natures of the gaseous and crystalline states are fairly well understood, but that of the liquid state is much more complex and has not been satisfactorily characterized at all. This project, then, was concerned with a study of the liquid state and its physical properties. Specifically, the properties studied were the viscosity, density, and ultrasonic velocity in liquids. Reid (34) states that there is a large need at present for more data and much better estimation techniques in the area of liquid viscosities, particularly for the estimation of liquid mixture viscosities.

Present Work

The purpose of this project was to serve as a pilot project of a series of research projects aimed at a better understanding of the liquid state. An empirical correlation between ultrasonic velocity and viscosity in nonassociated hydrocarbon liquid mixtures was sought. In addition, a correlation between ultrasonic velocity and density in liquid mixtures was of interest.

Another important contribution of this work was supplying a set of viscosity, density, ultrasonic velocity, and composition data for hydrocarbon liquid mixtures. This set of data may be used by others interested in the liquid state, instead of relying on obtaining data from several different sources using different experimental techniques and varying conditions of temperature and pressure. Five pure components, thirty binary mixtures, thirteen ternary mixtures, and four quaternary mixtures were chosen for study in this project at a pressure of 1 atm. and at temperatures of 25°C and 45°C. The five pure components were n-hexane, cyclohexane, benzene, ethylbenzene, and n-tridecane, all of which are nonassociated liquids. The mixtures were made up of these pure components.

CHAPTER II

PREVIOUS WORK

Before proceeding with a description of the work of this project, an examination of the efforts of earlier researchers would be instructive. The viscosity of a gas can be adequately described by stating that it is primarily dependent on momentum transfer in random molecular collisions. But the viscosity of a liquid results from the presence of strong intermolecular force fields, and is much more difficult to describe.

Andrade

One of the first significant breakthroughs in the study of liquid viscosities was the work of Andrade (1, 2) in 1934. He postulated that the theory of liquids should be approached not, as had been done before, from the point of view of the kinetic theory of gases, but from the point of view of the solid state, the density of which is not markedly different from that of the liquid state of the same substance. His reason for this approach was that the kinetic theory of gases was constructed to deal with matter where the spaces between the molecules are large compared with the size of molecules, whereas this isn't true of the liquid state close to the melting point.

Andrade stated that the forces between molecules in the solid and liquid states cannot be very different. Cited as support for this view was the theory of fusion which supposes that melting takes place when the amplitude of the vibrations of the molecules about their equilibrium positions becomes a fixed large fraction of the average distance between the atoms. The equilibrium is then disturbed and the substance becomes a liquid which has much in common with the solid while still in the vicinity of its melting point.

Andrade then considered a liquid as moving in plane layers parallel to one another, with a velocity gradient in the direction normal to the layers. He assumed that viscosity is due to a transfer of momentum from layer to layer as in Maxwell's theory of gaseous viscosity. However, this momentum transfer is not effected to any appreciable extent by a movement of the equilibrium position of molecules from one layer to another, but by a temporary union at the periphery of molecules in adjacent layers, due to their large amplitudes of vibration. Therefore, the molecules are considered, to a first approximation at least, to remain in their original layers while executing vibrations about a very slowly changing equilibrium position.

Andrade assumed that the arrangement of molecules in the liquid state is much like that in the solid state. Therefore the average intermolecular force which acts on a given molecule as the result of the electric field of its neighbor molecules is very little different from the average intermolecular force in the solid state. The principal difference between the liquid and solid states is not the magnitude of the intermolecular force under which the molecule vibrates, but the amplitude of the motion. This amplitude in the liquid state is so large that the molecules come into contact at the extreme of every oscillation. As a result, the molecules are disturbed and the "position of equilibrium" in the liquid is slowly displaced, whereas it is fixed in a solid. Therefore, the assumption is that a liquid molecule vibrates about a slowly displaced equilibrium position with a frequency which is the same as that of the molecule in the solid state.

Andrade further assumed that when, at every extreme oscillation, the molecules of one layer come into contact with those of an adjacent layer, they will usually at this contact enter into a temporary union. The duration of this union does not exceed the brief time necessary for the molecules to acquire a common velocity of translation. This duration must be very small compared to the period of vibration and does not involve what is ordinarily called association. This velocity sharing between molecules in adjacent layers will introduce viscous forces.

With the above two assumptions in mind, Andrade proceeded to express the viscosity of a simple liquid close to its melting point in terms of experimental constants having nothing to do with viscosity measurements:

$$\mu = 5.1 \times 10^{-4}(A_w T_m)^{1/2}/V_A^{2/3} \tag{1}$$

This equation predicts the viscosities of simple liquids (such as molten mercury, lead, tin, and copper) close to their melting points. It doesn't do well at all, however, for more complex liquids or for temperatures very far removed from the melting point.

Andrade went on to attempt to explain the temperature variation of viscosity, by saying that liquid viscosity decreases with temperature because the temperature agitation interferes with the interchange of momentum at the extreme oscillations. In the general case, all that he assumed, to account for temperature variation, was that a certain mutual potential energy of the juxtaposed molecules is necessary if momentum transfer is to take place in the direction normal to the line of centers. The number of cases favorable for transfer will decrease as the temperature rises, and the rate of decrease at a given temperature will depend upon the magnitude of the potential energy involved.

Based on the above assumptions, Andrade suggested the following approximate formula for the temperature variation of viscosity:

$$\mu = A \exp(c/T) \quad . \tag{2}$$

In order to take account of the variation of volume with temperature, he modified this formula to give:

$$\mu v^{1/3} = A \exp(c/vT) \quad . \tag{3}$$

This formula was used with some success in predicting the temperature variation of the viscosities of several simple organic liquids, but does not have wide application.

Eyring

Eyring (9), another early researcher interested in the liquid state, pictured a liquid as containing a number of holes moving about and playing the same part as molecules do in a gas. He postulated that the energy necessary to form a hole of molecular size in a liquid is equal to the energy of vaporization per molecule. He suggested the following two equations for the estimation of the "free volume" in a liquid:

$$v_f^{1/3} = \frac{c' R T V_T^{1/3}}{N^{1/3} \Delta E_{vap.}} \quad , \tag{4}$$

and

$$u = (V_T/Nv_f)^{1/3} (RT\gamma/M)^{1/2} \quad ; \tag{5}$$

where c' is a "packing number" defined by

$$v_f = c'^3 \left[(V_T/N)^{1/3} - d \right]^3 \quad . \tag{6}$$

After setting forth the "hole theory" as his working model of the liquid state, Eyring went on to say that the flow of a liquid is a rate process in that it takes place at a definite velocity. Therefore, he supposed that the theory of absolute reaction rates can be applied to viscosity. Accordingly from potential barrier arguments, he stated that the viscosity of a liquid varies with temperature in the following way:

$$\mu = B \exp(E_{vis.}/RT) \tag{7}$$

where B is some function of temperature and $E_{vis.}$ is the activation energy for flow. This activation energy consists of the energy required to form the hole and that required to move the molecule into the hole, the former contribution being by far the larger of the two.

In Eyring's hole theory, it is necessary for a molecule, after making a jump from one equilibrium position to the next, to remain at its new position long enough to dissipate the energy it possessed while passing over the energy barrier by staying at each potential-energy minimum until a Maxwellian distribution of energy is restored. If this condition is not fulfilled, then it would probably be more satisfactory to assume the mechanism to involve the transfer of momentum from one layer to the next by molecules passing back and forth between them.

In an attempt to correlate viscosity in terms of more familiar data than the activation energy for flow, while still using his hole theory, Eyring assumed that the fluidity of a liquid is proportional to the number of holes present in the liquid. To get a measure of the number of holes, he considered the essential difference between a solid and a liquid to be the introduction of holes. Therefore, $V_T - V_S$ is proportional to the number of holes in the liquid which is proportional to the fluidity, where V_T is the molar volume of the liquid at the temperature T, and V_S is the molar volume of the unexpanded solid. In equation form, this is

$$\phi = \frac{V_T - V_S}{a'} \quad . \tag{8}$$

For the case of hydrocarbons, Eyring writes equation (8) as

$$a'\phi = \frac{V_T - V_S}{V_S} \quad , \tag{9}$$

or

$$b\phi = v - a \tag{10}$$

in terms of the specific volume, where $v = V_T/M$, and a and b are constants. If the fluidity of a hydrocarbon depends only on the number of holes present in the liquid, then equation (10) indicates that a plot of v vs. ϕ would give a straight line for hydrocarbons, irrespective of temperature and pressure. Eyring found this to be true for paraffin hydrocarbons with up to fourteen carbon atoms. When the carbon atoms number more than fourteen, the viscosity is greater than would be indicated by equation (10), possibly because the unit of flow is smaller than the whole chain. For the molecule to flow, it is necessary for the movements of all the segments of the molecule to be coordinated, and the probability of this occurring will decrease as the length of the whole chain increases. Therefore, the viscosity is higher than if all the units were to move together automatically.

Eyring went on to consider the viscosities of associating liquids. He noted that the viscosities for associating liquids were much higher than those for analogous nonassociating substances, and that their values decrease rapidly with increasing temperature. A plot of log μ vs. 1/T is non-linear for associating liquids, and therefore the energy of activation for viscous flow is not independent of T. He postulated that there is a "structure activation energy" (a breaking of hydrogen bonds) in addition to the normal activation energy, for the flow of associated liquids. As the temperature is raised, there is a decrease in the number of H bonds that have to be broken before flow can occur, and hence the activation energy decreases.

To apply his theory of absolute reaction rates to binary mixtures, Eyring stated that the molar volume and activation energy for the mixture are molar additive functions of the pure component data, and that the excess free energy of mixing should be subtracted from the mixture activation energy. Accordingly, his equation for the fluidity of a binary mixture is

$$\phi = \frac{V_{mix.}}{hN} \exp\left[-(x_1\Delta E_1 + x_2\Delta E_2 - \Delta F_m)/2.45RT\right] . \qquad (11)$$

Eyring's work has gained wide acceptance, although he does have some detractors (12, 13). Suffice it to say here that his concepts have been used as the basis for the work of many others, and served the important function of awakening considerable interest in the nature of the liquid state. The concept behind equation (10) above figured importantly in the development of many of the later theories of the liquid state.

Recently, Eyring and co-workers have developed the concept of "significant liquid structures". These significant structures are said to be of three types: (1) gas-like molecules; (2) solid-like molecules; and (3) molecules exhibiting an intermediate positional degeneracy. Eyring assumes that holes of molecular size are overwhelmingly abundant because

> (a) they confer gas-like properties on a neighboring molecule jumping into the hole and (b) a solid-like molecule obtains a positional degeneracy equal to the number of neighboring vacancies. (9)

Then, if one neglects any increase in volume due to holes of other than molecular size, the number of holes per mole of molecules is $(V_T - V_S)/V_S$, as in equation (9) above. Assuming that the chance of a vacancy conferring gas-like properties on a neighboring molecule is proportional to the fraction of neighboring positions populated by molecules, then for random distribution of vacancies the mole fraction of gas-like molecules is $(V_S/V_T)(V_T - V_S)/V_S = (V_T - V_S)/V_T$. The solid-like molecules comprise the remaining mole fraction, V_S/V_T. Therefore, Eyring's equation for the viscosity of a liquid takes the form:

$$\mu = \frac{V_S}{V_T}\mu_S + \frac{(V_T - V_S)}{V_T}\mu_g \qquad (12)$$

where μ_S and μ_g are the contributions of the solid-like and gas-like molecules, respectively, to the total viscosity. Eyring's expressions for μ_S and μ_g have been successfully applied only to very simple liquids like argon. It is important to note here that Eyring stressed the fact that he did not picture the liquid state as being a mixture of solid and gas. But rather, a liquid molecule has solid-like properties during the time it vibrates about an equilibrium position, then it instantly becomes gas-like in behavior as it jumps into a vacancy.

Frenkel

In 1932, J. Frenkel (8) proposed a theory to explain liquid structure and the transport properties of liquids that was probably the first vacancy theory of liquids. It was based on the idea that the perturbations of order in a monatomic crystal can be reduced to the formation of holes, i.e., vacant sites of a crystal lattice, and that melting takes place when the relative number of such holes reaches a certain limiting value defined in a more or less arbitrary way. Since fusion is usually accompanied by a relatively small increase of volume, say about 10%, Frenkel reasoned that the molecular arrangement in liquids must be similar to that in solids, at least in the vicinity of the melting point. Thus, in spite of the fundamental difference between the amorphous structure of liquids and the crystalline structure of solids, Frenkel maintains that the difference between liquids and solids is of a quantitative nature and not a qualitative one.

Thus, Frenkel denotes the structure of liquids by the term "quasi-crystalline" in the sense that they display a certain degree of local order of the same type as that characteristic of the corresponding crystals. In the case of simple liquids the degree of local order can be judged from the average distribution of the atoms about one of them. This "relative" distribution, according to Frenkel, must be independent of the choice of the central atoms and must be spherically symmetrical with respect to it.

Frenkel then stated that the homogeneity of a liquid is only apparent and not real, to a certain extent, and that in reality liquids contain a large number of surfaces of rupture. In the absence of external forces these surfaces do not develop to macroscopic size, but are spontaneously closed up in some places only to open again in adjacent locations. Thus, at any instant, the body of a liquid constitutes a system of microscopic cavities in the form of holes and cracks.

If the above is true, then the free volume of a liquid is not distributed uniformly among all its molecules as in the case of crystals, but is concentrated in the form of separate micro-cavities, or holes. The appearance and disappearance of such holes is a result of fluctuations connected with the heat motion of the liquid.

From this point of view, Frenkel contends that it is meaningless to treat the viscosity of a liquid as the result of a transfer of momentum by the individual atoms, since the momentum of each atom cannot be considered as a constant of the motion, as in the case of gases, but oscillates rapidly along with the vibrations of the atom about its equilibrium position. Then Frenkel makes a statement that is very important if one is to understand the course of his work with the theory of liquids:

> The fact to be explained in the case of liquids is _not their viscosity_, that is the resistance to shearing

stress, but rather their fluidity, i.e. the capability of yielding to such a stress. (8)

In order to put his theory into equation form, Frenkel states that the fluidity of a liquid must be proportional to the mobility of the individual particles constituting it. Since the mobility, according to Einstein's relation, is proportional to the diffusion coefficient, then the viscosity is inversely proportional to it. If the self-diffusion coefficient of a liquid is proportional to $\exp(-E_{vis.}/kT)$, then the viscosity of a liquid is represented by

$$\mu = A \exp(E_{vis.}/kT) \qquad (13)$$

with a slightly temperature-dependent coefficient A.

McAllister

In a recent publication, McAllister (28) presented a correlation for the kinematic viscosity of binary liquid mixtures based on Eyring's theory of absolute reaction rates. He started with Eyring's equation for the variation of absolute viscosity with temperature, and stated it in terms of the kinematic viscosity and the free energy of activation:

$$\nu = \frac{hN}{M} \exp(\Delta G/RT) \qquad (14)$$

where ΔG is the molal free energy of activation for viscosity.

McAllister proposed that the free energies of activation for viscosity are the additive quantities. To give expression to the total free energy of activation as the sum of several component parts, he considered a binary mixture of molecules of types 1 and 2. He further stipulated that these molecules undergo only three body interactions in one plane. He said that such three body interactions in one plane are valid if the radii of the two types of molecules differ by less than an arbitrary factor of 1.5. If the factor were more than 1.5, then it would be necessary to consider interactions involving more than three molecules on a three-dimensional basis.

Assuming that the probability for the interactions is dependent only on the concentration and not on the free energy of activation, the types of interactions are 1-1-1, 1-2-1, 2-1-1 (and 1-1-2), 2-1-2, 2-2-1 (and 1-2-2), and 2-2-2, while their respective fractions of total occurrences are x_1^3, $x_1^2x_2$, $2x_1^2x_2$, $x_1x_2^2$, $2x_1x_2^2$, and x_2^3. If one further assumes that ΔG is the same for the three types of interactions involving two molecules of type 1 and one of type 2 denoted as ΔG_{12}, and likewise for ΔG_{21}, then the equation for ΔG is

$$\Delta G = x_1^3\Delta G_1 + 3x_1^2x_2\Delta G_{12} + 3x_1x_2^2\Delta G_{21} + x_2^3\Delta G_2. \qquad (15)$$

Substituting equation (15) and molar average molecular weights into equation (14), taking the natural logarithms of the various terms, and combining, yields McAllister's final equation:

$$\ln\nu = x_1^3\ln\nu_1 + 3x_1^2x_2\ln\nu_{12} + 3x_1x_2^2\ln\nu_{21} + x_2^3\ln\nu_2 - \ln(x_1 + x_2M_2/M_1) + 3x_1^2x_2\ln\left[(2 + M_2/M_1)/3\right] + 3x_1x_2^2\ln\left[(1 + 2M_2/M_1)/3\right] + x_2^3\ln(M_2/M_1). \tag{16}$$

Note again that equation (16) is for a three-body interaction, planar model of a binary mixture in which the radii of the two types of molecules differ by a factor of less than 1.5. For a mixture such as acetone plus water, in which the size ratio is 1.61, McAllister states that a seven- or eight-body interaction, three-dimensional model would be necessary to properly describe its viscosity behavior.

If McAllister's equation is applied within its realm of definition, it gives quite good results. But the following points should be kept in mind when considering its use: (a) one must have values for the interaction terms (ν_{12} and ν_{21}) for each binary mixture, and for each combination of temperature and pressure; (b) in order to calculate ν_{12} and ν_{21}, a knowledge of mixture and pure component kinematic viscosities is necessary; (c) if many calculations were to be made, it would be necessary to use a computer, and computer use would be imperative if a four-body or higher order interaction, three-dimensional model were necessary; and (d) if absolute viscosities are desired, mixture density data must be available.

Jacobson

When considering liquid properties, such as viscosity, which are dependent on intermolecular processes, an essential concern must be the distance between molecules. Yet most investigators and theoreticians ignore this parameter when attempting to describe the liquid state, even though much is done with mean free paths in gases. There is good reason for this evasion, of course. The intermolecular distance in liquids is a very difficult parameter to define quantitatively. Liquid molecules are constantly changing position, and if a molecule were very irregular in shape, the question would arise: from what point on a molecule does one measure its distance from another one?

One of the men who addressed himself to this problem was Jacobson. In a series of articles, Jacobson (16, 17, 18, 19, 20, 21, 22) described his concept of the "intermolecular free length" and its applications to the study of the intermolecular processes in liquids. He concerned himself with such liquid properties as compressibility, surface tension and viscosity. If these properties are designated by the letter j, then Jacobson states that they follow the simple relation

$$j = k'L^p \tag{17}$$

where k' and p are constants for each property and temperature irrespective of composition, structure, size and shape of the molecules in the liquid or liquid mixture.

Jacobson defines the intermolecular free length as

$$L = \frac{2V_a}{Y} = \frac{2(V_T - V_o)}{Y} \tag{18}$$

where V_a, the available volume, is equal to the difference between the molar volume V_T at the temperature T and the molar volume V_o at the temperature at which the fluidity (inverse of the viscosity) is zero. Y is the molecule surface of one mole of the liquid, which Jacobson defines as

$$Y = (36\pi N V_o^2)^{1/3}. \tag{19}$$

Note that Jacobson's "available volume" is similar to Eyring's "free volume".

The velocity of ultra sound in a liquid is principally determined by its intermolecular properties. The simplest intermolecular property is the intermolecular free length, so Jacobson proposed a relationship between it and ultrasonic velocity. He let j in equation (17) be the adiabatic compressibility, β_{ad}, and found that

$p = 2$ at room temperature using experimental values of β_{ad}. He equated this expression for β_{ad} to the well known expression $\beta_{ad} = 1/u^2\rho$, and found that

$$uL\rho^{1/2} = K(T) \qquad (20)$$

where K(T) is a slightly temperature dependent constant. Jacobson found that values of L calculated from equations (18) and (20) agreed within a few per cent when experimental data for 55 nonassociated organic liquids and five series of liquid mixtures were used for the calculations. He did not state which liquids were tested. He felt that this was a significant result in that it enabled researchers to use ultrasonic velocity data when studying intermolecular phenomena.

Since Y in equation (18) is a surface area, it is obvious that Jacobson's L is the average distance between the surfaces of molecules. A comment at this point on why he choose this distance instead of that between centers of attraction would be in order. Intermolecular forces consist of attractive forces and repulsive forces. The attractive forces depend on the distance between centers of attraction, which do not coincide with the geometrical centers of the molecules and are very difficult to define. On the other hand, repulsive forces depend on the distance between the surfaces of the molecules, which has a clear physical significance and is therefore easier to define clearly.

When attempting to calculate L from equation (17), using $j = \phi$, Jacobson discovered rather large errors in L when compared to values calculated from the definition, equation (18). He determined empirically that he could obtain better results if ϕ were plotted as directly proportional to L and inversely proportional to some power of M, the molecular weight. He tried 1/2 and 1/3 as the powers of M, among others, and found quite good agreement between values of L obtained in this way and those calculated from the definition.

Because of the rather controversial and speculative nature of the liquid state, there are almost as many theories to explain it as there are people who are interested in doing so. The above five approaches serve as interesting examples of the way some of these people view the liquid state, and any further attempt to explain other theories here would merely belabor the point.

Ultrasonic Transmission in Liquids

By definition, ultrasonic sound waves are those which have frequencies which are higher than any that a human can hear (above about 16 kc/s). The study of ultrasonics may be divided into two parts, one concerned with low-amplitude vibrations and the other with high energies. Low-amplitude waves are used for non-destructive testing, when one is concerned with the effect of the medium on the waves. An example of this type of testing is the measurement of the propagation constants of the ultrasonic wave through the medium, such as velocity and absorption coefficient. High energy waves are used to cause changes in the medium by the waves, and examples are cleaning and drilling.

Ultrasonic frequencies are used for these purposes instead of audio-frequencies for several reasons, among which are: (a) plane wave conditions are more easily realized with the shorter wavelengths; (b) absorption coefficients are usually higher and therefore easier to measure; and (c) higher frequency waves are easier to focus.

There is a linear relationship between the applied stress and the resultant strain when low-amplitude waves are used, and thus Hooke's law is followed. When attempting to correlate propagation constants with other physical constants of a substance, plane waves should be used. Plane waves originate from a plane surface source which is vibrating in simple harmonic motion. If the source vibrates in a direction parallel to the wave motion, it produces longitudinal waves, called compression waves because they give rise to alternate compressions and rarefactions. When the motion of the source is normal to the wave motion direction, the propagated waves are called transverse waves. In bulk media, transverse waves cause alternating shear stresses and are thus called shear waves, although not all transverse waves are shear waves.

Sound waves are characterized by their wave vectors which periodically vary in value with both space and time. The wave vectors of plane waves at a particular time have constant values everywhere in a plane normal to the direction of sound propagation. If the waves are longitudinal, the wave vectors are oriented in the direction of propagation. If they are transverse, the wave vectors are polarized in a direction normal to that of the wave motion.

Plane waves are attenuated by deviation of energy from the parallel beam by regular reflection, refraction, diffraction, and scattering, and by absorption, in which case mechanical energy is converted into thermal energy by internal friction. Absorption losses can yield valuable information about the physical properties of the substance through which the sound wave propagates. Scattering attenuation gives information about grain sizes in polycrystals and the densities and sizes of aerosols and hydrosols. In cases where the attenuation is uniform everywhere in the acoustic field, it can be characterized by the absorption coefficient.

At megacycle frequencies, the most common type of absorption is the relaxational type. Energy is absorbed during the positive half of the stress cycle, and is given up during the negative half of the cycle, usually during a finite period of time. If thermal energy (from absorption losses) is applied to one part of a liquid, so that its temperature is raised, energy may flow to other parts of the liquid until equilibrium is established. The amount of energy transferred from the sonic wave to any particular part of the liquid increases exponentially with time to a final value and is characterized by a finite time constant, called the relaxation time.

At comparatively low frequencies, attenuation is negligible. As the frequency is increased, the absorption increases to a maximum value at the relaxation frequency, and then decreases to zero at a very high frequency. At this high frequency, there isn't enough time for any energy to be exchanged between parts of the liquid. Because of this lack of energy exchange, the medium becomes "stiffer" and therefore there is an increase in the modulus of elasticity. Since the sonic velocity is proportional to the square root of the elasticity, then it must increase also. This velocity change with frequency is called velocity dispersion.

Cavitation is another phenomenon that must be considered when propagating sonic waves through liquids. Cavitation occurs in those regions of a liquid which are subjected to rapidly alternating, high amplitude pressures. When a sonic wave travels through a liquid, the liquid undergoes compression during the positive half of the pressure cycle, and is subjected to a tensile stress during the negative half-cycle. Any bubbles present in the liquid will be alternately expanded and contracted. A bubble will collapse suddenly during the compression if the pressure amplitude is sufficiently high and the initial radius of the bubble is less than a certain critical value. This sudden collapse is known as cavitation, and it results in an almost instantaneous release of a comparatively large amount of energy (heat, and sometimes light).

Cavitation can also occur in gas-free liquids when the acoustic pressure amplitude exceeds the hydrostatic pressure in the liquid. One may induce cavitation in a gas-free liquid by introducing defects in its lattice structure by adding impurities or by bombarding the liquid with neutrons. The threshold of cavitation is the minimum intensity (watts/cm^2) or amplitude required to produce cavitation. The threshold intensity usually increases as pressure increases, but decreases as temperature increases.

A device used to generate or receive a sonic wave is called a transducer. Some of the types of transducers are: (a) crystal oscillators, utilizing the piezoelectric and electrostrictive effects, which have wide ranges of frequencies up to about 10,000 Mc/s; (b) magnetrostrictive oscillators with an upper frequency limit of 100 kc/s; (c) electromagnetic transducers, with an upper limit of 50 kc/s; and (d) electrostatic transducers, with an upper limit of 100 kc/s.

Since the crystal oscillators are the most common and versatile ultrasonic transducers, the two effects they utilize will be briefly discussed here. The first of these two effects is the piezoelectric effect. If a slab is cut from a crystal having axes of non-symmetry with its parallel surfaces lying normal to an axis of non-symmetry, then equal and opposite electric charges appear on the parallel surfaces when the slab is subjected to a mechanical stress. This is called the piezoelectric effect, and the opposite can also occur, i.e., when an electric field is applied in the direction of an axis of non-symmetry the slab is mechanically strained. Typical crystals exhibiting this effect are quartz, Rochelle salt, tourmaline, and lithium sulphate.

The electrostrictive effect occurs in all dielectrics (materials which permit the passage of the lines of force from an electrostatic field, but are nonconducters), but is negligible for most materials except ferroelectrics, in which it is a pronounced effect. When an electric field is applied to this type of material in a given direction, a mechanical strain is produced. The magnitude of this mechanical strain is proportional to the square of the applied field strength and therefore is independent of the sense of the field. Thus a positive strain occurs for both positive and negative values of the exciting field.

A polarized ferroelectric transducer appears to display the piezoelectric effect, and therefore is commonly referred to as being piezoelectric. Barium titanate and lead zirconate are widely used electrostrictive substances. Many small crystallites of ferroelectric material are mixed with suitable additives to form a ceramic transducer of the required size and shape. Such a transducer, being polycrystalline, has an advantage over a natural piezoelectric crystal in that it is isotropic and does not have to be cut along a particular axis.

CHAPTER III

APPARATUS AND EXPERIMENTAL PROCEDURES

Pure Liquids and Mixtures

The pure liquids studied in this project were n-hexane, cyclohexane, benzene, ethylbenzene, and n-tridecane. These pure grade (99 mole % minimum purity) chemicals were supplied by the Special Products Division of Phillips Petroleum Co., Bartlesville, Oklahoma. These compounds are all nonassociated, but comprise a representative group of hydrocarbons that will make an interesting initial study in this field. They include a short straight chain hydrocarbon, an intermediate length straight chain hydrocarbon, an aromatic, a substituted aromatic, and a saturated ring compound.

The binary, ternary, and quaternary mixtures for this study were made up from the above pure components. Mixtures having compositions of 25% - 75%, 50% - 50%, and 75% - 25% were prepared for each of the ten possible binary combinations of the pures, where all compositions are in mole percent.

The four pures to be used for the quaternaries were chosen (deleting benzene from the above five), and ternary mixtures were prepared from them. For each of the four possible three-component combinations, ternary mixtures were made up at compositions of 50% - 25% - 25%, 25% - 50% - 25%, and 25% - 25% - 50%. In addition, one ternary mixture was made up containing benzene, the component deleted from the other ternaries. This mixture contained 50% benzene, 25% ethylbenzene, and 25% cyclohexane. The four quaternary mixtures contained compositions of 40% - 20% - 20% - 20%, 20% - 40% - 20% - 20%, 20% - 20% - 40% - 20%, and 20% - 20% - 20% - 40% of n-hexane, cyclohexane, ethylbenzene, and n-tridecane, respectively.

A Model B6 Mettler Analytical Balance, with a range of 0 to 100 gm., was used to prepare the mixtures. This is a precision analytical balance which reports weights to the nearest 0.00001 gram. The compositions determined from these weighings were reported correct to the nearest 0.0001 mole fraction.

Constant Temperature Bath

A pressure of one atmosphere and temperatures of 25°C and 45°C were chosen for this study. Therefore, a constant temperature bath filled with water and open to the atmosphere was entirely adequate. A large (2 ft. in diameter) glass cylinder was chosen as the vessel for the bath. A Tecam Tempunit TU8 (Techne (Cambridge) Ltd., Duxford, Cambridge, England), a combination heater, thermostat, stirrer, and centrifugal pump, was used as the heater-controller mechanism for the bath. It was mounted in such a position that the centrifugal pump discharged tangentially to the walls of the bath vessel in order to achieve the best circulation. This unit controlled the bath temperature to within ± 0.01°C at 25°C and to within ± 0.02°C at 45°C.

A copper coil was placed in the bath and cooling water was circulated through it by a Sargent Water Bath Cooler (E. H. Sargent and Co., Chicago, Cat. No. S-84890, Serial No. 1207006). The thermometers used were #F3324 and #C3227 (Brooklyn Thermometer Co., Inc.) covering the ranges 18°C to 30°C and 34°C to 46°C respectively. These thermometers were 3 ft. long and were graduated in divisions of 0.01°C. They were calibrated by the manufacturer to read 25.00°C and 45.00°C respectively to the nearest 0.01°C. These calibrations were checked against a platinum resistance thermometer and found to be correct.

Pycnometers

The pycnometers used in this investigation, based on the design of Robertson (37), were Model JB-2250 Robertson pycnometers (Scientific Glass Apparatus Co., Inc., Bloomfield, N. J.) graduated in 0.001 ml from 0 to 0.05 ml. They were calibrated with degassed, double distilled water at both 25°C and 45°C. These pycnometers had a whole range of graduations from which to read the volume, instead of the single hash-marks of many other pycnometers (see Figure 1), and were thus much easier to use.

The pycnometers were weighed dry and partially evacuated and then weighed after being filled to some point on the graduations. With the weight of the liquid contained in each of the two pycnometers thus determined, they were placed in the constant temperature bath for thirty minutes. At the end of this time, the caps were removed briefly to allow the liquid levels in the two arms to equalize, and a scale reading was made. This scale reading gave the volume of the liquid in the pycnometer. In order to determine whether or not there was any significant evaporative loss when the caps were removed, a series of tests was made in which they were left off for various lengths of time, the shortest time being the actual operating condition. No difference in the densities of several of the pures was noticed even for periods of time 3 times as long as the actual operating time.

From the weights and volumes thus determined, the liquid densities were calculated. If the densities calculated using the two pycnometers differed by more than 0.0002 gm/cc for a particular liquid, the results were discarded and new tests were made. In almost all

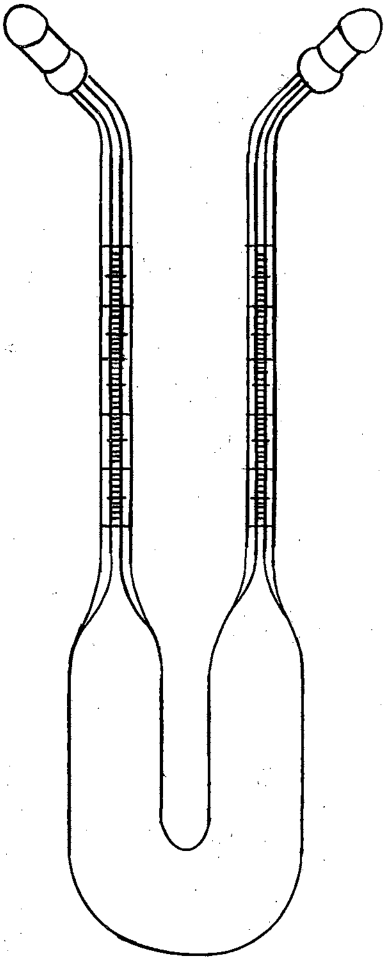

Figure 1. Drawing of the Modified Robertson Pycnometer

of the cases studied, the two pycnometers agreed to within 0.0001 gm/cc.

There was no need to correct for the weight of the air in the arms of the pycnometers over the liquid, because in the very worst case (scale reading = 0.00), the effect on the densities would be about ± 0.00002 gm/cc. Since the densities were to be reported to the nearest fourth decimal place, the effect of the weight of the air in the arms was negligible.

Viscometers

The viscometers used in this project were Model C-50 Cross Arm Type Universal Viscometers (California Laboratory Equipment Co., Berkeley, California). These viscometers are commonly called Zeitfuchs Cross Arm Viscometers (23). The kinetic energy, surface tension, and drainage errors for this type of viscometer are too small within the range of the viscometer to be conveniently measured (23). Within the range of the viscosities measured in this study, there were no corrections to be made, since none was large enough to affect the reported viscosity values.

The viscometers were calibrated using the National Bureau of Standards' calibrating oil D. The constants of the viscometers for use in equation (21) were determined to be 0.00996 and 0.03002 at both 25°C and 45°C.

With the viscometer supported on a level surface in the constant temperature bath, the sample was introduced into the viscometer at A (see Figure 2) and allowed to flow into the horizontal tube B until the meniscus was on the line C. The liquid was allowed two minutes to attain temperature equilibrium at this point, even though it had been determined previously that one minute was a sufficient residence time (23). After this time suction was applied at D, which caused the liquid to flow into the capillary. The passage of the meniscus was timed between lines E and F with a Model T-101 electronic timer (Nuclear Instrument and Chemical Corp., Chicago).

This time was read to the nearest 0.005 min. with the electronic timer and the kinematic viscosity calculated from the equation

$$\nu = Ct \tag{21}$$

where ν is the kinematic viscosity in centistokes, C is the viscometer constant, and t is the time in seconds. This procedure was repeated until the times measured in two successive runs agreed within 0.005 min. This agreement was usually accomplished in two runs, but occasionally three runs had to be made.

Ultrasonic Apparatus

The ultrasonic transmitter used in this research was a Sonomedic Biosonar 200 (Sonomedic Corp., now

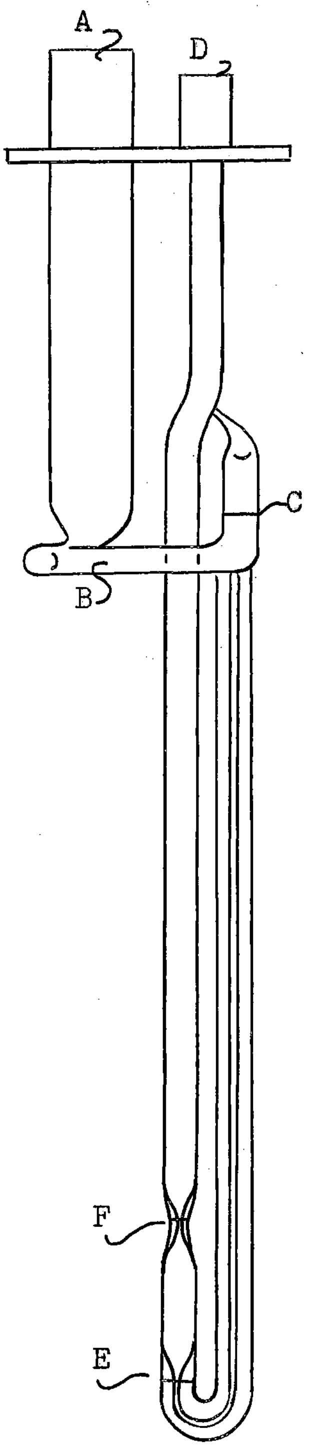

Figure 2. Zeitfuchs Cross Arm Viscometer

defunct). Because of poorly grounded electrical lines, it was necessary to pass the electricity through an isolation transformer between the electrical outlet and the transmitter (see Figure 3). To further reduce the effects of "line noise" on the operation of the ultrasonic transmitter, it was operated between 6:00 p.m. and 8:00 a.m. when most of the fluorescent lights and pieces of electrical apparatus in the building were not in use.

The transmitter operated at a frequency of 1 Mc/s (invariable), and delivered pulses to the transmitting transducer at a rate of 1000 pulses per second (also invariable). These pulses were 2 microseconds wide. The average power input to the transducer was about 0.5 watt/cm^2. The transducers used in this work were thin wafers of barium titanate, which display the electrostrictive effect.

The transducers were situated at either end of a cylindrical aluminum sample cell containing the liquid to be studied. At a specific instant a pulse was sent by the transmitter to the transmitting transducer and at the same time a counter was activated by a start gate on the back of the transmitter. This ultrasonic pulse traveled through the liquid to the receiving transducer, which then retransmitted the pulse. The number of times the pulse traveled between the two transducers was registered as cycles/sec. on a Model 201C Frequency-Period

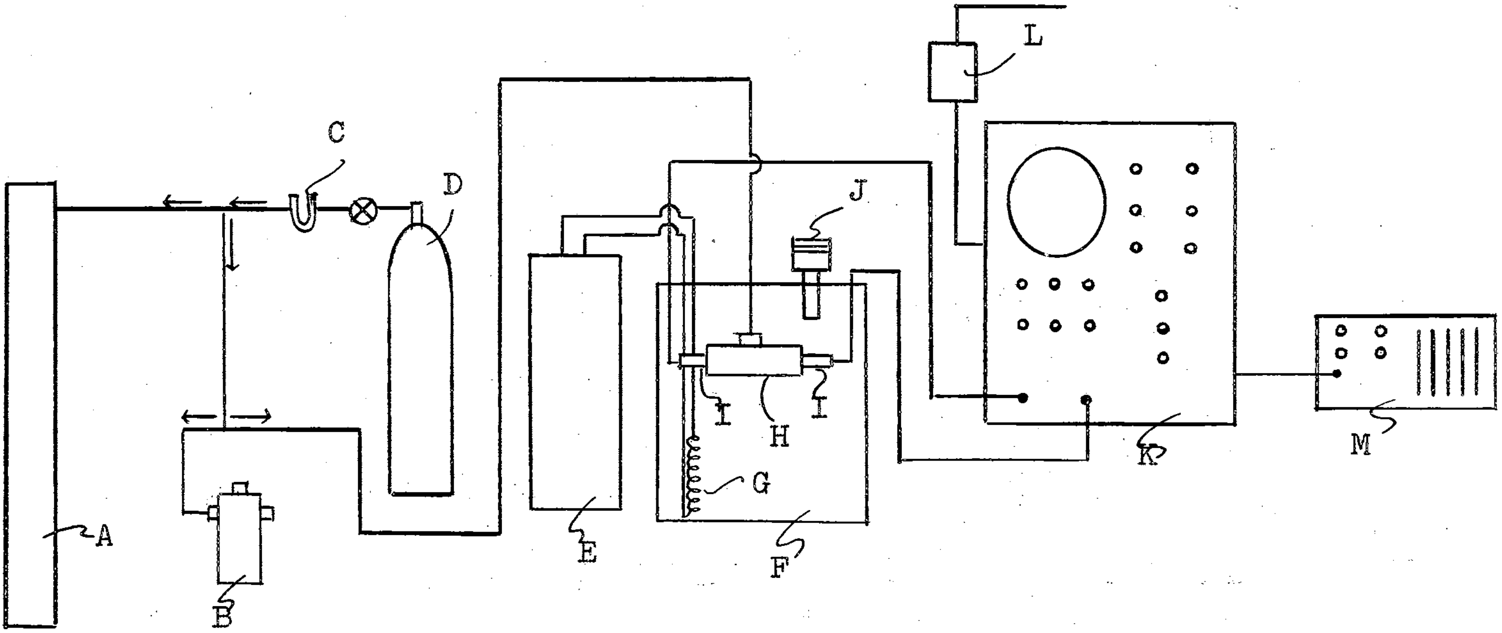

Figure 3. Schematic Diagram of the Experimental Apparatus for Measuring the Ultrasonic Velocity in Liquids

TABLE I

LEGEND FOR FIGURE 3

A. Manometer
B. Cartesian Manostat
C. Desiccant-filled U-tube
D. Bottle of dry nitrogen
E. Circulating water cooler
F. Water filled, glass, constant temperature bath
G. Cooling coil
H. Container for liquid to be studied
I. Transducers
J. Heater, stirrer, and temperature controller
K. Ultrasonic pulse generator
L. Isolation transformer
M. Pulse counter

Counter (Computer Measurements Co.). This experimental setup is known as the pulse-type method. Other methods are described in the literature (3, 31, 35).

A constant pressure of 1 atm. was maintained in the sample cell by applying pressure from a cylinder of nitrogen sufficient to make up the difference between 1 atm. and actual atmospheric pressure. This constant pressure was maintained by a Model No. 8 Cartesian Manostat (Manostat Corporation, New York).

The liquid sample was poured into the sample cell, and the cell was then connected to the constant pressure system and immersed in the constant temperature bath. The Depth Window Opening Open and Gain controls on the transmitter were adjusted until the best possible pulse trace appeared on the oscilloscope. It is possible that there were small changes in composition during the time that the mixtures were in the sample cell. However, the ultrasonic data were reproducible using various residence times of the liquid in the sample cell, so whatever composition changes that did occur did not affect the ultrasonic data.

The sample was allowed to remain in the constant temperature bath for 30 minutes at 25°C and for 45 minutes at 45°C. Thereafter, the counter reading was noted every 15 minutes until the same reading (to four significant figures) was obtained three times in succession. The pulse trace on the oscilloscope was checked after each reading until the best trace was found at a particular setting of the Gain control twice in succession. The counter reading in cycles/sec. was converted into ultrasonic velocity in m/sec. by multiplying by the distance between the transducers (m/cycle). This distance was determined by calibrating the sample cell with benzene, the pure component in this study for which the best ultrasonic data was available (31).

CHAPTER IV

RESULTS AND DISCUSSION

As stated in the Preface, this project was concerned with gaining a better insight into the liquid state. Of special interest was attempting to establish a relationship between viscosity and ultrasonic velocity in non-associated hydrocarbon liquid mixtures. Also of interest was a correlation between density and ultrasonic velocity in the same mixtures. As the literature survey progressed, a critical lack of consistent sets of density, viscosity, and ultrasonic velocity data for liquid mixtures became apparent. Therefore, another contribution of this project was producing such a set of data.

Density

The density measurements were the most accurate performed in the course of this research project. When the measured densities of the pure components were compared with those of Rossini (38) they agreed in most cases to within 0.0001 gm/cm^3, with a mean error of 0.028%. This small a difference could easily be attributed to differences in the purities of the liquids used by Rossini and those of the present work. An examination of the curves of density as a function of composition in Figures 9 through 18 reveals no unusual variation of density with composition. Most of the curves are linear, and the others are very nearly linear. These density values are reported with an experimental confidence of ± 0.0001 gm/cm^3. The work of Ridgway and Butler (36) provides a comparison for the density data of this project at 25°C for the binary systems n-hexane—cyclohexane, n-hexane—benzene, and cyclohexane—benzene. The two sets of data were virtually identical for all three binary systems.

Two rather simple correlations for the density of liquid mixtures as a function of ultrasonic velocity were found in the literature, those of Rao (32) and Wada (45). Rao correlated density and ultrasonic velocity with the equation

$$\frac{u^{1/3}M}{\rho} = R' \qquad (22)$$

where M is the molecular weight and R' is Rao's constant. Rao found this constant to be independent of temperature and specific for each particular liquid. He also found that R' was an additive function on a molar basis for liquid mixtures.

Rao stated that the constant R' for a liquid may be regarded as the molecular volume of the liquid when the velocity of sound in it is unity. Since molecular volumes of liquids at the boiling point are molar additive functions, and since R' can be regarded as a molecular volume when the velocity of sound in the liquid is unity, then Rao supposed that the same additivity would apply to the constant R'. This proved to be the case for the liquid mixtures that Rao studied (he did not state what these mixtures were).

Rao plotted his values of R' vs. the molecular weight of successive members of homologous series of compounds. He found these curves to be straight, parallel lines. Therefore, values of R' for any homologous series may be calculated from an equation of the form

$$R' = \alpha M + \beta \quad . \tag{23}$$

Rao's values for α and β are given in Table XII in Appendix B.

Rao's correlation was applied to the mixture data of this work, using molar averages of M and R' and the experimental ultrasonic velocities were predicted with an absolute average deviation of 1.14% at 25°C (Table IX) and an absolute average deviation of 0.82% at 45°C (Table X). This agreement was so good that no time was spent attempting to obtain another density-ultrasonic velocity correlation.

Wada's correlation is merely a modification of that of Rao:

$$W = \frac{Mu^{2/7}}{\rho^{6/7}} = M^{1/7} (R')^{6/7} \quad . \tag{24}$$

This correlation also fits the experimental data well, but not as well as Rao's, and it is more difficult to use for calculations. Therefore, Rao's correlation was chosen as the better of the two.

Viscosity

When compared with the viscosity values of Rossini (38), the viscosity data for the pure components in this work show an absolute average deviation of 0.62%. The viscosity data in this work are reported with an experimental confidence of 0.0005 centipoise. The work of Ridgway and Butler (36) provides a comparison for the viscosity data of this project at 25°C for the binary systems n-hexane—cyclohexane, n-hexane—benzene, and cyclohexane—benzene. The two sets of data agreed very well for all three binary systems, as may be seen in Figures 19, 20, and 23.

The curves of viscosity as a function of composition in Figures 19 through 28 show both negative and positive deviations from linear behavior. These deviations from linearity are small except in the cases of the cyclohexane—benzene and cyclohexane—ethylbenzene mixtures, where slight minima are noted (Figures 23 and 24). These positive and negative deviations from ideality may be explained in the case of associated liquid mixtures by examining the excess entropy functions for the mixtures (39). This explanation does not apply to the data of this work, however, since excess entropy functions for nonassociated liquids are either negligible or zero.

A possible explanation of the minima in the viscosity curves of Figure 23 might be that the initial effect of adding benzene to cyclohexane is the weakening of the dispersion forces between the cyclohexane molecules, just as adding benzene to a hydrogen-bonded liquid such as acetic acid breaks up the hydrogen-bonding. At higher concentrations of benzene, the effect of the planar benzene molecules' ability to lie closer together than the non-planar cyclohexane molecules takes precedence. Then the viscosity of the mixture increases with the concentration of benzene. A similar explanation could apply to the minima in the viscosity curves of Figure 24.

As stated in Chapter II, the intermolecular free length was chosen as the correlating parameter for a correlation between viscosity and ultrasonic velocity in nonassociating hydrocarbon liquid mixtures. Jacobson (16) postulated that simple relations exist between the intermolecular free length in a liquid and its properties which are dependent on intermolecular processes. These properties, which include compressibility, surface tension, and viscosity, were said by Jacobson to follow the simple relation

$$j = k'L^p \tag{17}$$

where j is the particular property of interest, L is the intermolecular free length, and p and k' are constants for each property and temperature irrespective of composition, structure, size and shape of the molecules in the liquid or liquid mixture.

Jacobson defines the intermolecular free length as

$$L = \frac{2V_a}{Y} = \frac{2(V_T - V_o)}{Y} \tag{18}$$

where V_a, the available volume, is equal to the difference between the molar volume V_T at the temperature T and the molar volume V_o at the temperature at which the fluidity (inverse of the viscosity) is zero. $Y = (36\pi N V_o^2)^{1/3}$ is the molecule surface of one mole of the liquid, where N is Avogadro's number.

Since the ultrasonic velocity u in a liquid is principally determined by the intermolecular properties of the liquid, a correlation between u and L is a definite possibility. Jacobson (16) has proposed such a relation:

$$uL\rho^{1/2} = K(T) \quad . \tag{20}$$

Equation (20) is the relation used to calculate values of L from the ultrasonic velocity data of this work. K(T) is a function of temperature only, regardless of chemical composition. The values used for K(T) in this work were

625 at 25°C and 647 at 45°C (17). Other values for K(T) may be found in Table XI in Appendix B.

The fluidity ϕ was found to be a better correlating parameter than the viscosity, as suggested by Frenkel. The experimental fluidities from this study were plotted against L, $L/M^{1/3}$, and $L/M^{1/2}$, as suggested by Jacobson's work, the third method proving to be the best. The molecular weights of the mixtures were computed on a molar average basis for this application. Substituting the expression for L from equation (20) into $L/M^{1/2}$, the plot is now ϕ plotted against $K(T)/u\rho^{1/2}M^{1/2}$.

Since a correlation was desired between viscosity and ultrasonic velocity only, ϕ was plotted against $L\rho^{1/2}/M^{1/2}$, or $K(T)/uM^{1/2}$, to eliminate the density. Therefore, the correlation in this form is:

$$\frac{1}{\mu} = k_1\left[\frac{K(T)}{uM^{1/2}}\right] + c_1 \quad . \qquad (25)$$

This correlation was applied to the data of this project and plotted in Figures 4 and 5. These plots gave values of $k_1 = 57.14$ and $c_1 = -1.3$ at both 25°C and 45°C. Using these constants, equation (25) predicted the experimental fluidities with an absolute average deviation of 15.54% at 25°C and an absolute average deviation of 13.61% at 45°C.

Examination of Figures 4 and 5 indicates rather wide scatter of the fluidity data when plotted as a function of $K(T)/uM^{1/2}$. Since it is only a function of temperature, K(T) is probably not flexible enough to be valid for a wide range of chemical compounds. The author felt that it might be instructive to calculate values to replace K(T), called K', for each pure component and mixture to give strict adherence of the experimental data to the curves of Figures 4 and 5. The problem then becomes one of determining a suitable equation for predicting values of K'.

In the search for characterizing parameters to predict K', recollection of proposed correlations between ultrasonic velocity and thermodynamic properties suggested the acentric factor, ω . The acentric factor is widely used as a parameter to predict the deviations from ideality of thermodynamic properties. Values of the pure component acentric factors for the compounds of this work were obtained from Erbar (6) and Reid and Sherwood (33), and molar average acentric factors were calculated for the experimental mixtures. When the values of ω for the experimental mixtures were plotted as a function of the calculated values of K', the data roughly described four parallel lines, arranged in order of increasing molecular weights. A plot of the molar average molecular weights of the experimental mixtures as a function of the calculated values of K' again roughly described four parallel lines.

Accordingly, a correlation of K' as a function of

ω and M appeared to have possibilities. In order to retain temperature dependence, K(T) was included in the correlation for K', which has the form:

$$K' = K(T) + a_1 + a_2\omega + a_3M \quad . \tag{26}$$

Multiple linear regression of the K' values calculated for the experimental pure components and mixtures showed that equation (26) can be used to predict K'. Values obtained for a_1, a_2, and a_3 were 312.59, 2602.4, and -10.432, respectively, at 25°C, and 356.51, 2722.98, and -11.057, respectively, at 45°C.

Substitution of K' as predicted by equation (26), for K(T) in equation (25) produced the proposed correlation in its final form:

$$\frac{1}{\mu} = k_1\left[\frac{K'}{uM^{1/2}}\right] + c_1 \quad . \tag{27}$$

This correlation was applied to the experimental fluidity data of this work and plotted in Figures 6 and 7, using the same values of k_1 and c_1 used in Figures 4 and 5. Equation (27) predicted the experimental fluidities with absolute average deviations of 9.79% at 25°C and 9.10% at 45°C (see Tables VI and VII in Appendix A). Note that in Tables VI and VII, the ternary and quaternary data fit the correlation better than the average in the majority of the cases.

The author was interested in applying the correlation of equation (27) to some data from the literature. A rather exhaustive search of the literature for ultrasonic velocity and viscosity data at the same temperature for nonassociated hydrocarbon liquid mixtures produced no results at all. So, density and viscosity data under the same conditions were sought, with the idea in mind that values of the ultrasonic velocity would be calculated from equation (22). In this case, values of R' for the pure components were estimated with equation (23), see Table XIII, and the mixture values of R' were the usual molar averages of the pure component values.

Not very many data points were produced by this search (44 points from 6 binary mixtures), but they proved to be enough to show the interesting possibilities of equation (27). In some cases the density and viscosity data for a particular mixture were not from the same source. Even so, when ϕ was plotted against $K'/uM^{1/2}$ for these mixtures, the literature fluidities were predicted with an absolute average deviation of 10.74% (see Table VIII and Figure 8). The circled points in Figure 8 are for mixtures of benzene and methyl ethyl ketone, the latter being an associating non-hydrocarbon. These points do not follow the curve in Figure 8, and are therefore not properly described by equation (27). In the case of mixtures containing an associating component, consideration must be given to the degree of association and equation (27) modified accordingly, as in the work of Ellis (5).

Considering all the data points together, from this experimental work and from the literature, equation (27) predicted 148 values of fluidity with an absolute average deviation of 9.83%. For a comparison with a correlation currently being used in industry for liquid hydrocarbon mixture viscosity predictions, the work of Lohrenz, et al. may be considered (27). They used a complicated empirical relation which had to be solved on a digital computer. Their correlation predicted experimental viscosities with an absolute average deviation of 16%, and they considered this to be good agreement. Ellis considered the extension of the correlation of the present work to associated liquid mixtures (5).

Correlating the viscosities and ultrasonic velocities of liquid mixtures with equation (27) shows definite possibilities. The ranges of chemical compounds and temperatures studied need to be extended considerably before this is said to be a universal correlation, however.

Ultrasonic Velocity

Two factors which must be taken into account when considering ultrasonic velocity data in liquids are cavitation and velocity dispersion as a result of relaxation. Blitz (3) shows the variation of threshold intensity (watts/cm^2) for cavitation as a function of ultrasonic frequency for water at room temperature on page 200. According to this information, the energy input to the system of the present work would have to be about 1000 times as high as it was in these experiments in order to induce cavitation in water. Water cavitates at lower intensities at a given frequency than organic liquids because it has a higher surface tension. Therefore, there were no cavitation problems in this study. Figure 2.5 in Blitz indicates that there were no velocity dispersion problems in the present work either, since the frequency of this work is on the linear part of the velocity curve adjacent to the ordinate.

Reliable ultrasonic velocity data for comparison purposes were not available in the literature for some of the pure components studied in the present work. However, it was evident that the experimental values for n-hexane and the binary mixtures containing n-hexane were much too high. The ultrasonic velocity in n-hexane should be much lower than that in any of the other pure liquids studied. It was somewhat lower, but still too high by about 200 m/sec., according to data from another source (35). Because of this, Rao's correlation was used to calculate values of u for mixtures 1 through 12, and the literature value was used for pure hexane, for the purposes of applying equation (27). This was considered legitimate because of the excellent predictions of u obtained with Rao's correlation for the other mixtures.

The only readily apparent explanation for the bad data for hexane and several other low velocity liquids which gave similar results is one of apparatus limitations. The ultrasonic transmitter used in this project was made as a medical diagnostic tool, and as such had a very narrow range of application since the human body is mostly water. The pulse rate and frequency in this apparatus were invariable. Such limitations would not be a handicap if only a narrow range of velocities were to be measured. However, when absorption losses occur, the frequency must be changed in order to eliminate them. If the frequency cannot be changed, the recorded ultrasonic velocity for the liquid sample will be too high. This is believed to be what happened in the cases of n-hexane and mixtures 1 through 12. Also, if the pulse rate is too high for the low velocity measurements, this can cause the counter to count secondary pulses as well as primary ones, resulting in a count that is much too high. The experimental confidence reported on the other pure components and mixtures was ± 5 m/sec.

Figures 33 and 34 exhibit the same minima in the cyclohexane—benzene and cyclohexane—ethylbenzene systems at 25°C for ultrasonic velocity as a function of composition as was noticed for viscosity as a function of composition. These minima may be explained the same way as were those in Figures 23 and 24. At 45°C, however, these minima are no longer present in Figures 33 and 34, and the curves are seen to be almost linear. Evidently at the higher temperature the molecules are far enough apart that the ability of the planar benzene molecules to lie closer together than the non-planar cyclohexane molecules takes precedence over the dispersion force field effects over the entire range of composition. Recall that when discussing viscosity curves one considers both the intermolecular force fields retarding the flow and the proximity of the molecules which can be a result of these force fields and/or a result of steric hindrance. Since ultrasonic propagation is a mechanical vibration in the liquid, one considers the intermolecular spacing regardless of the factors influencing it.

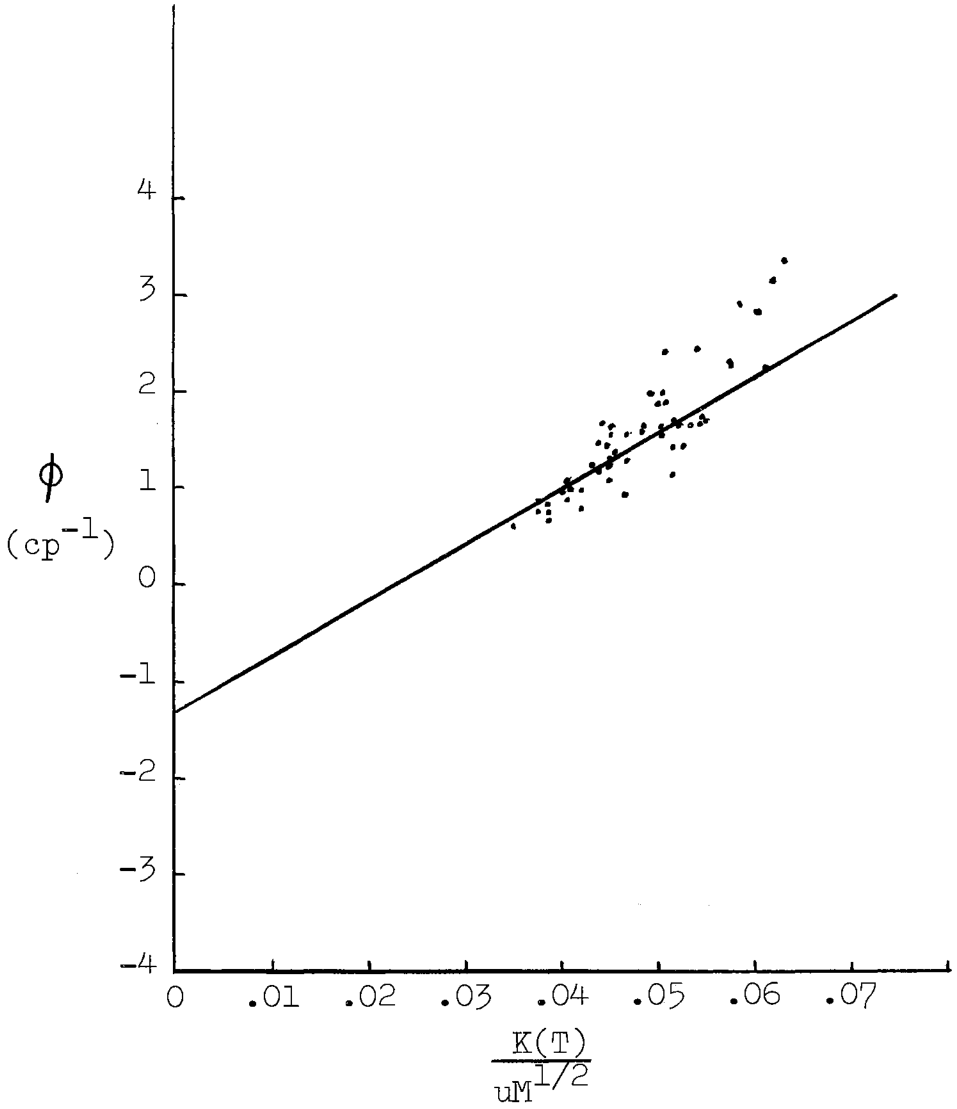

Figure 4. Experimental Fluidities as Inverse Functions of Ultrasonic Velocity at 25°C Using Equation (25)

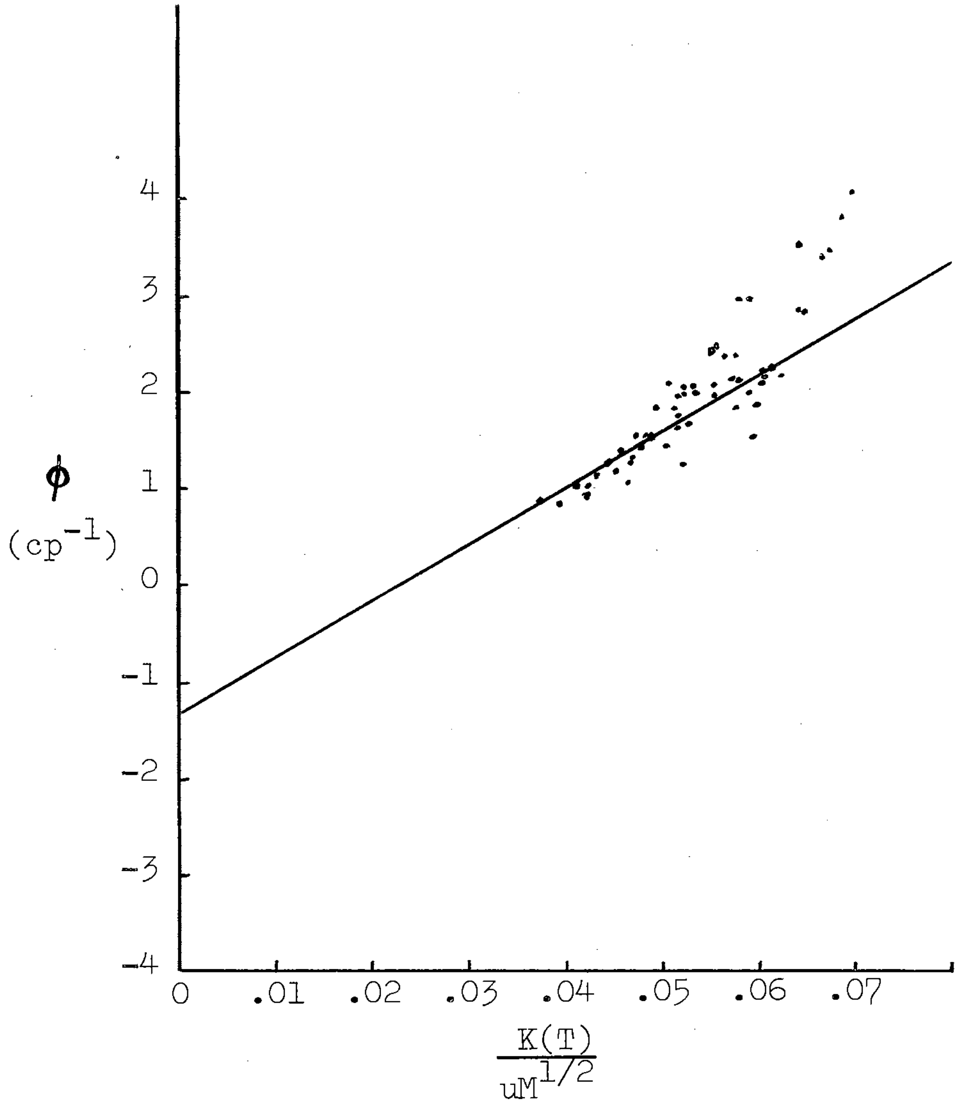

Figure 5. Experimental Fluidities as Inverse Functions of Ultrasonic Velocity at 45°C Using Equation (25)

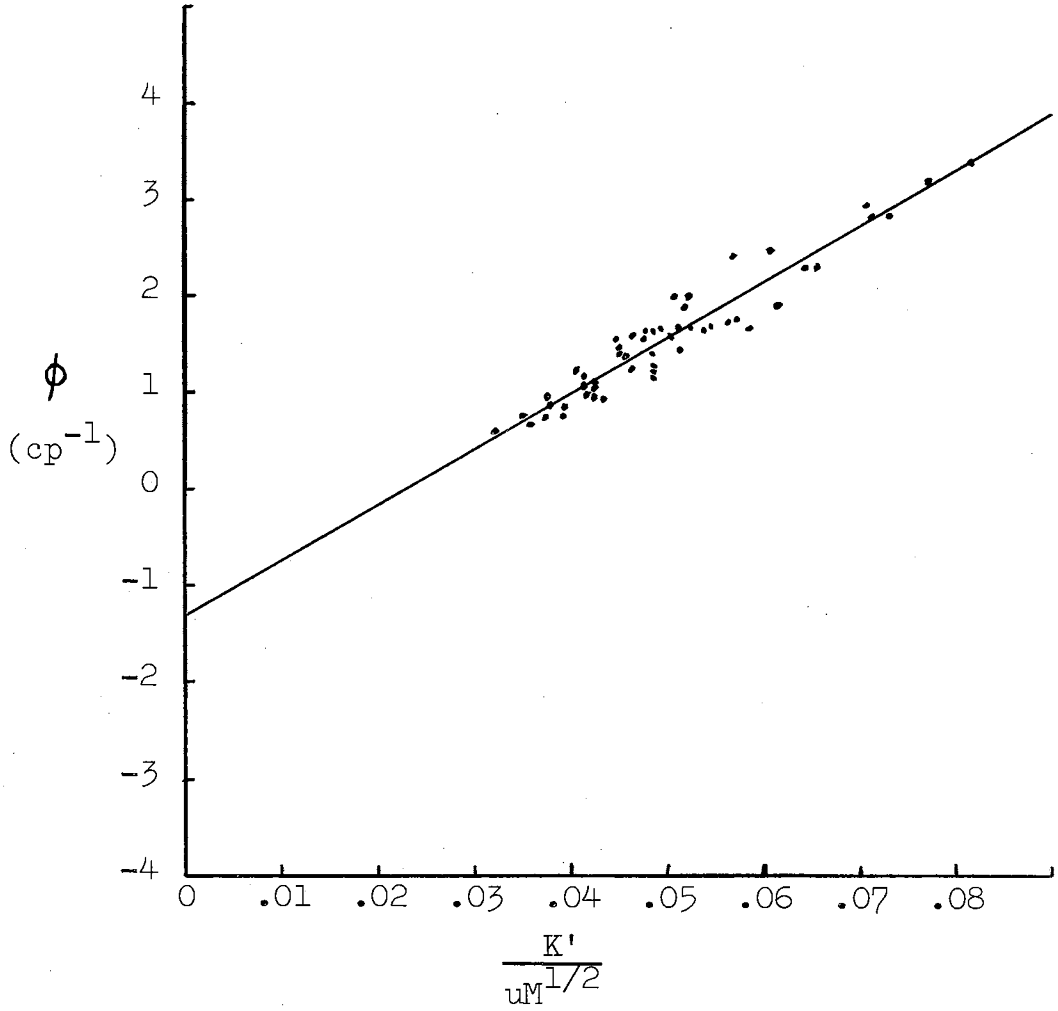

Figure 6. Experimental Fluidities as Inverse Functions of Ultrasonic Velocity at 25°C Using Equation (27)

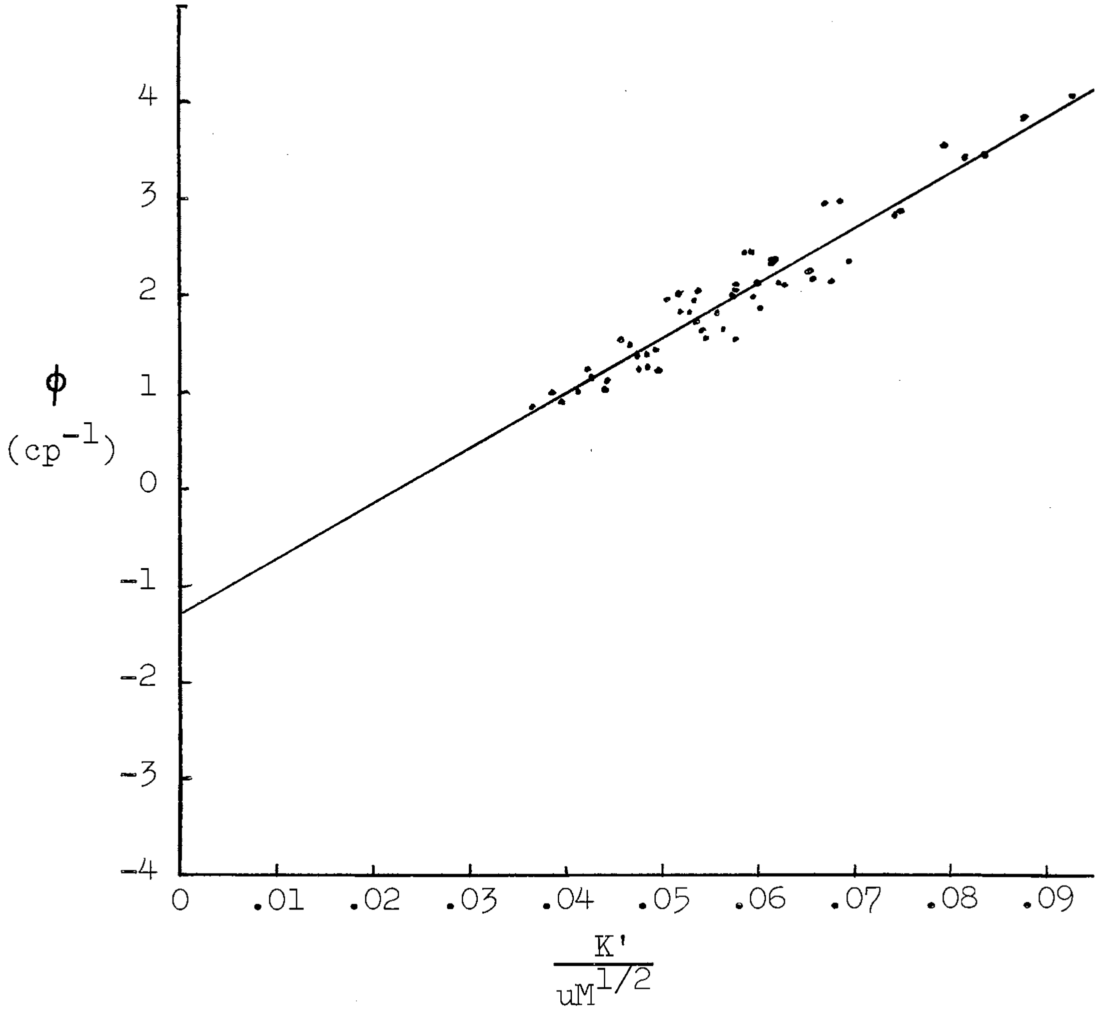

Figure 7. Experimental Fluidities as Inverse Functions of Ultrasonic Velocity at 45°C Using Equation (27)

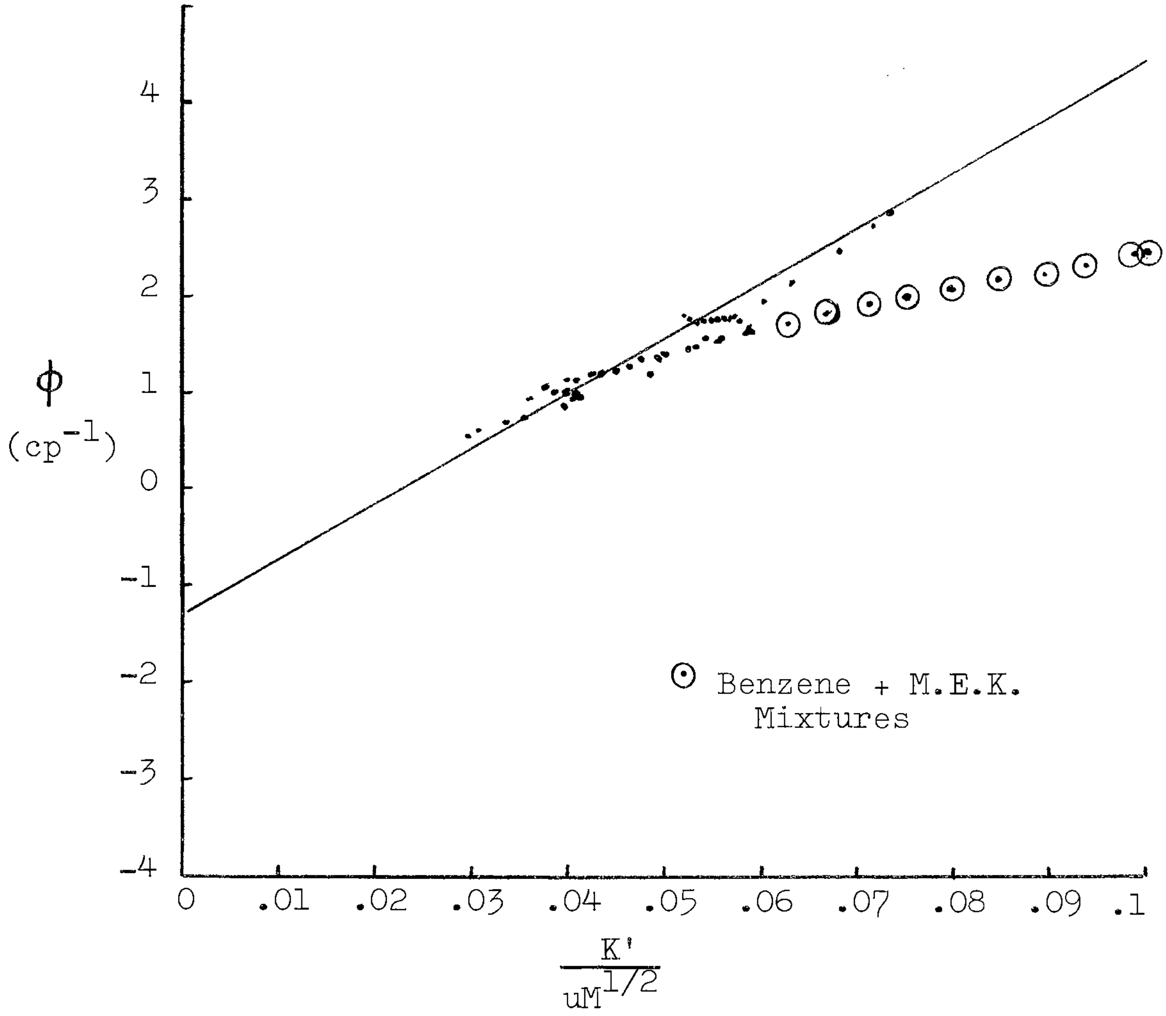

Figure 8. Literature Fluidities as Inverse Functions of Ultrasonic Velocity at 25°C Using Equation (27)

CHAPTER V

SUMMARY

A consistent set of density, viscosity, and ultrasonic velocity data has been gathered at a pressure of one atmosphere and at temperatures of $25^{\circ}C$ and $45^{\circ}C$. This set of data was obtained for n-hexane, cyclohexane, benzene, ethylbenzene, and n-tridecane, and for 30 binary, 13 ternary, and 4 quaternary mixtures of these five pure components.

A correlation between ultrasonic velocity and viscosity in nonassociated hydrocarbon liquid mixtures has been presented and tested for pure liquids and binary, ternary, and quaternary mixtures. The correlation has the form:

$$\frac{1}{\mu} = k_1\left[\frac{K'}{uM^{1/2}}\right] + c_1 \quad , \qquad (27)$$

where $K' = K(T) + a_1 + a_2\omega + a_3M$. Experimental fluidities were predicted with absolute average deviations of 9.79% at $25^{\circ}C$ and 9.10% at $45^{\circ}C$. Equation (27) was also applied to 44 data points from 6 binary mixtures from the literature, and predicted the literature fluidities with an absolute average deviation of 10.74%.

Correlating the viscosities and ultrasonic velocities of liquid mixtures with equation (27) shows definite possibilities. The ranges of chemical compounds and temperatures studied need to be extended considerably before this is said to be a universal correlation, however. This project was designed as a pilot project, and as such suggests many areas for further study.

Recommendations

(1) The range of liquids under study needs to be extended to include other types of compounds, such as halogenated hydrocarbons and amines.

(2) The temperature and pressure ranges must be extended, particularly the temperature range, in order to be certain of the form of the correlation presented in this work.

(3) In order to carry out the above two suggestions, it will be necessary to obtain another device for measuring ultrasonic velocities with a wider range of applicability.

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APPENDIX A

EXPERIMENTAL DATA
AND
CALCULATED VALUES

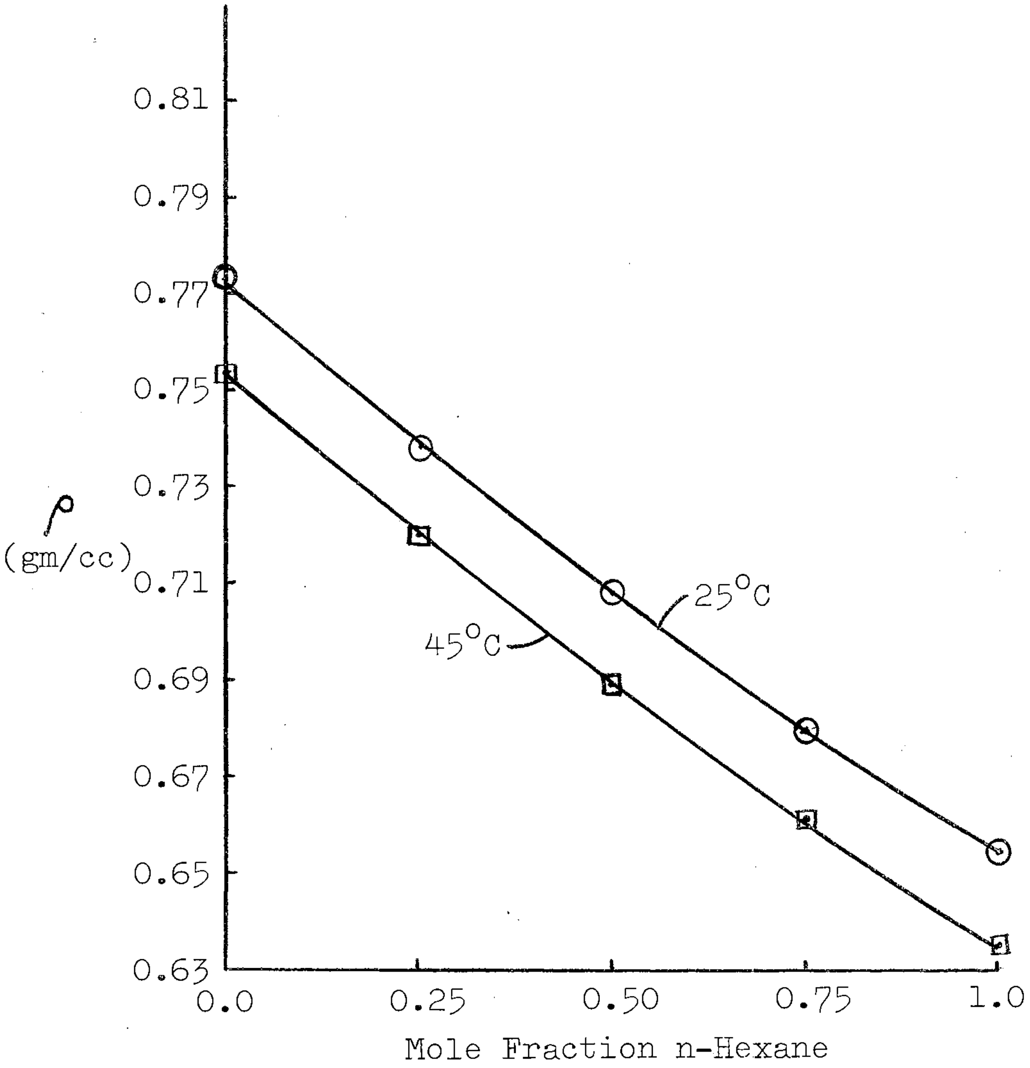
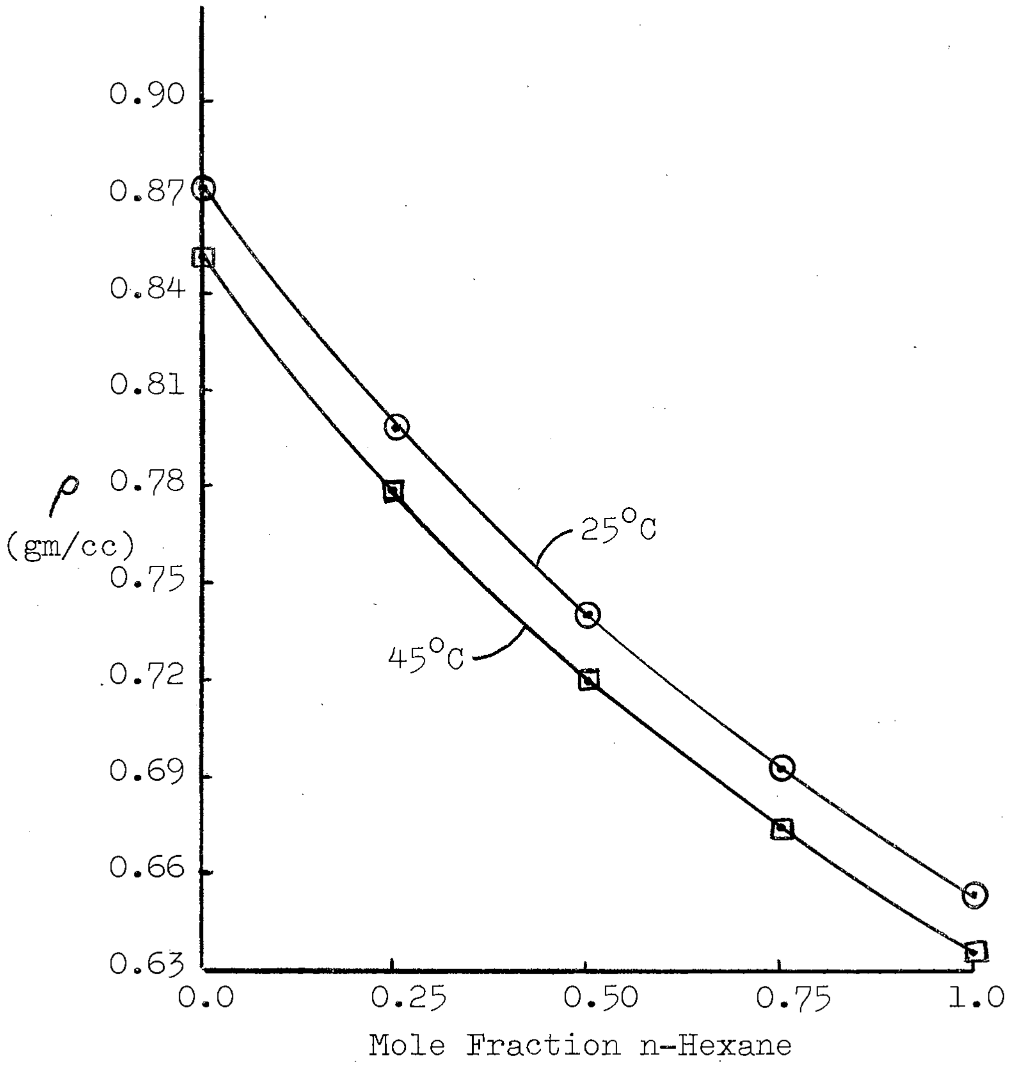


Figure 9. Effect of Composition on Density for the n-Hexane—Cyclohexane Binary System



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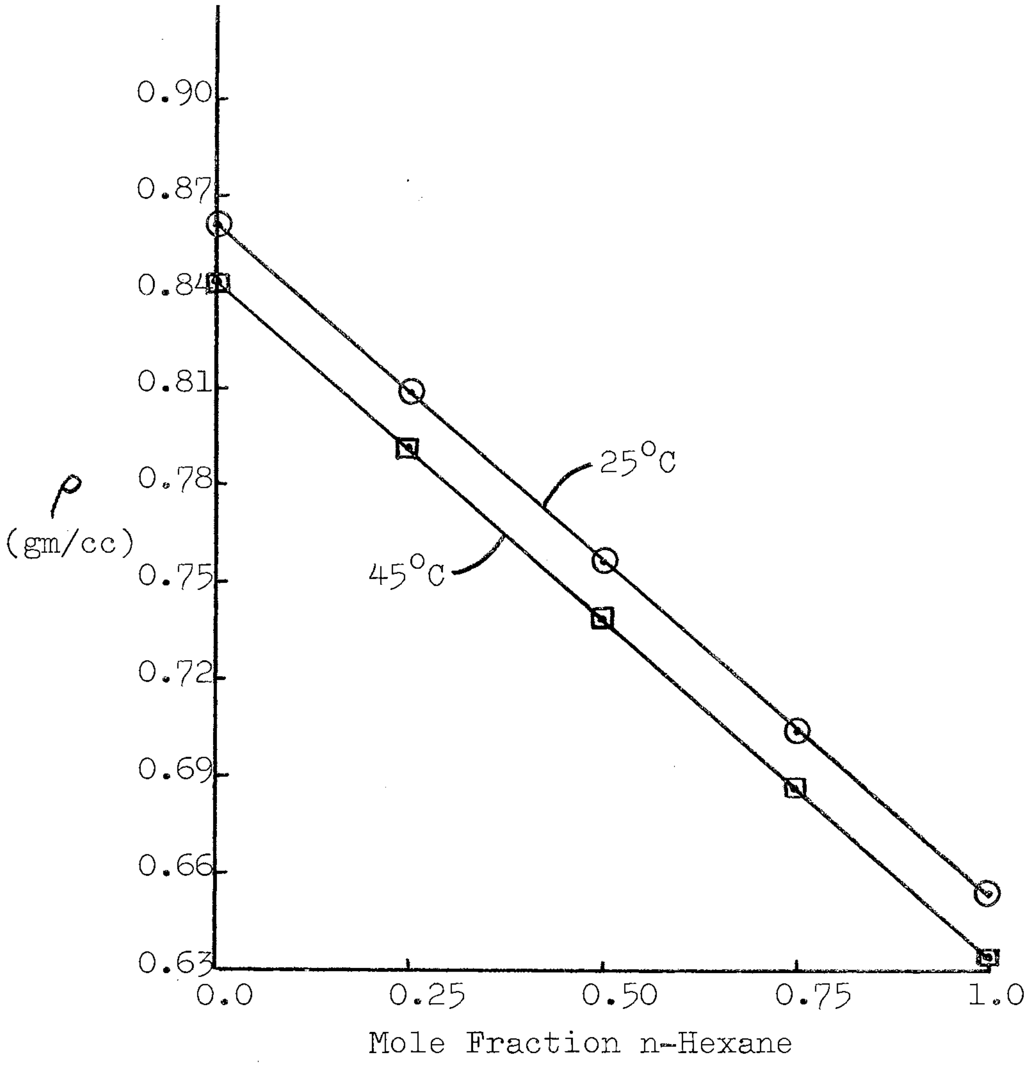


Figure 11. Effect of Composition on Density for the n-Hexane—Ethylbenzene Binary System

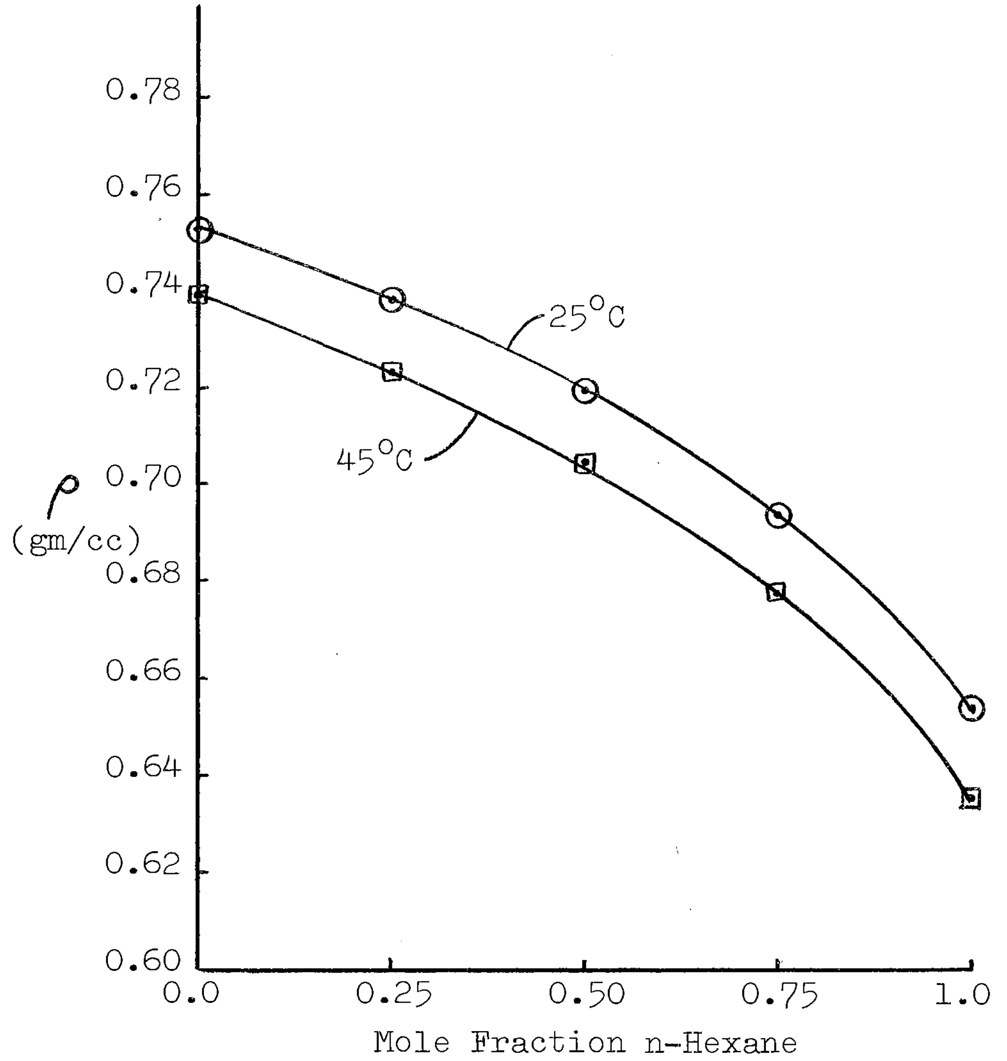
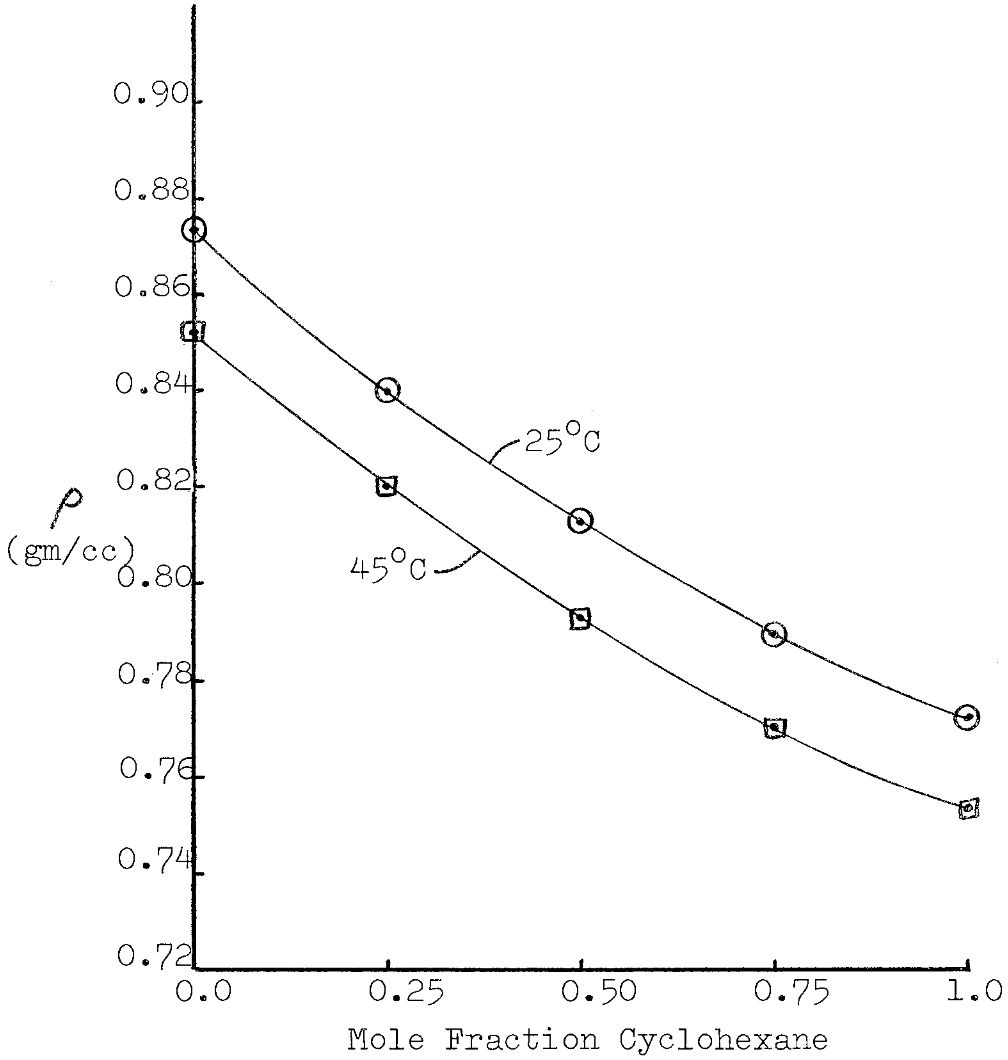


Figure 12. Effect of Composition on Density for the n-Hexane—n-Tridecane Binary System



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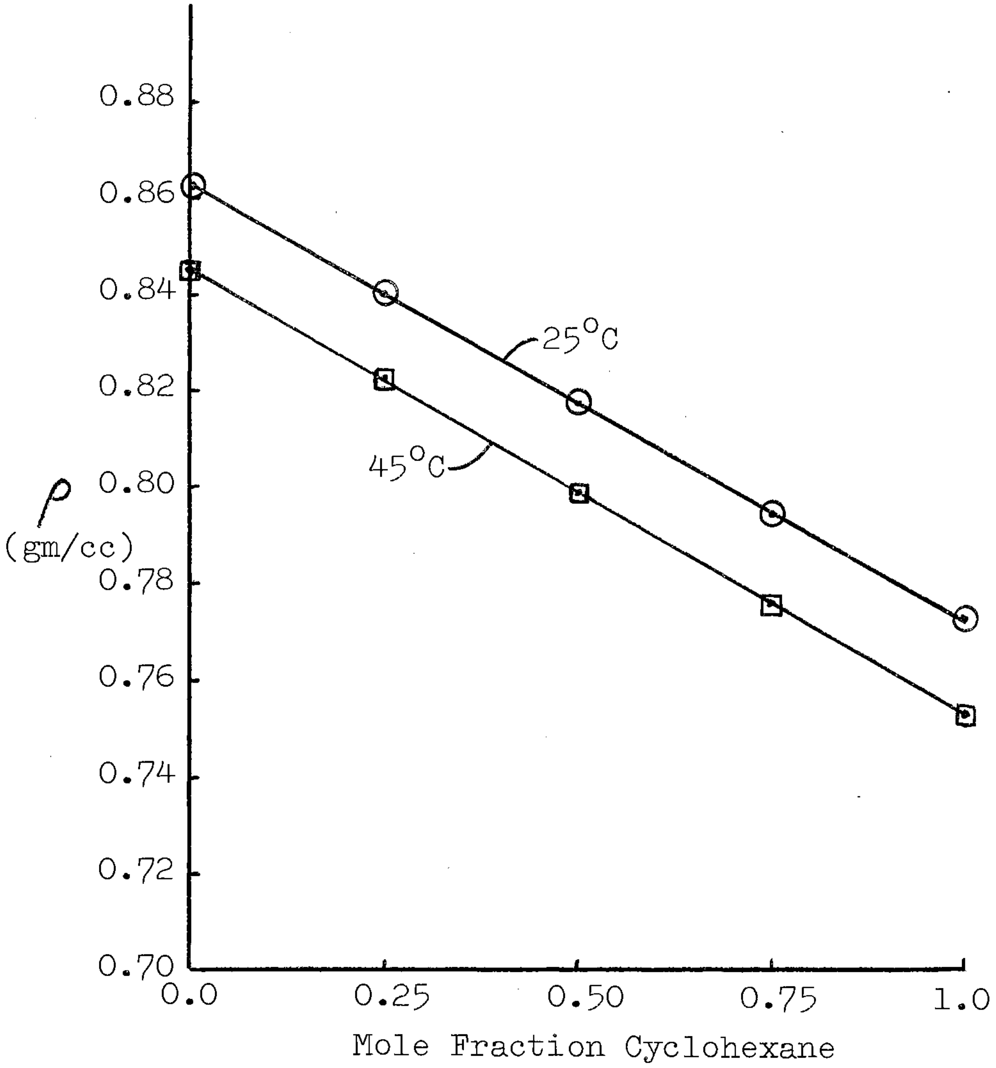

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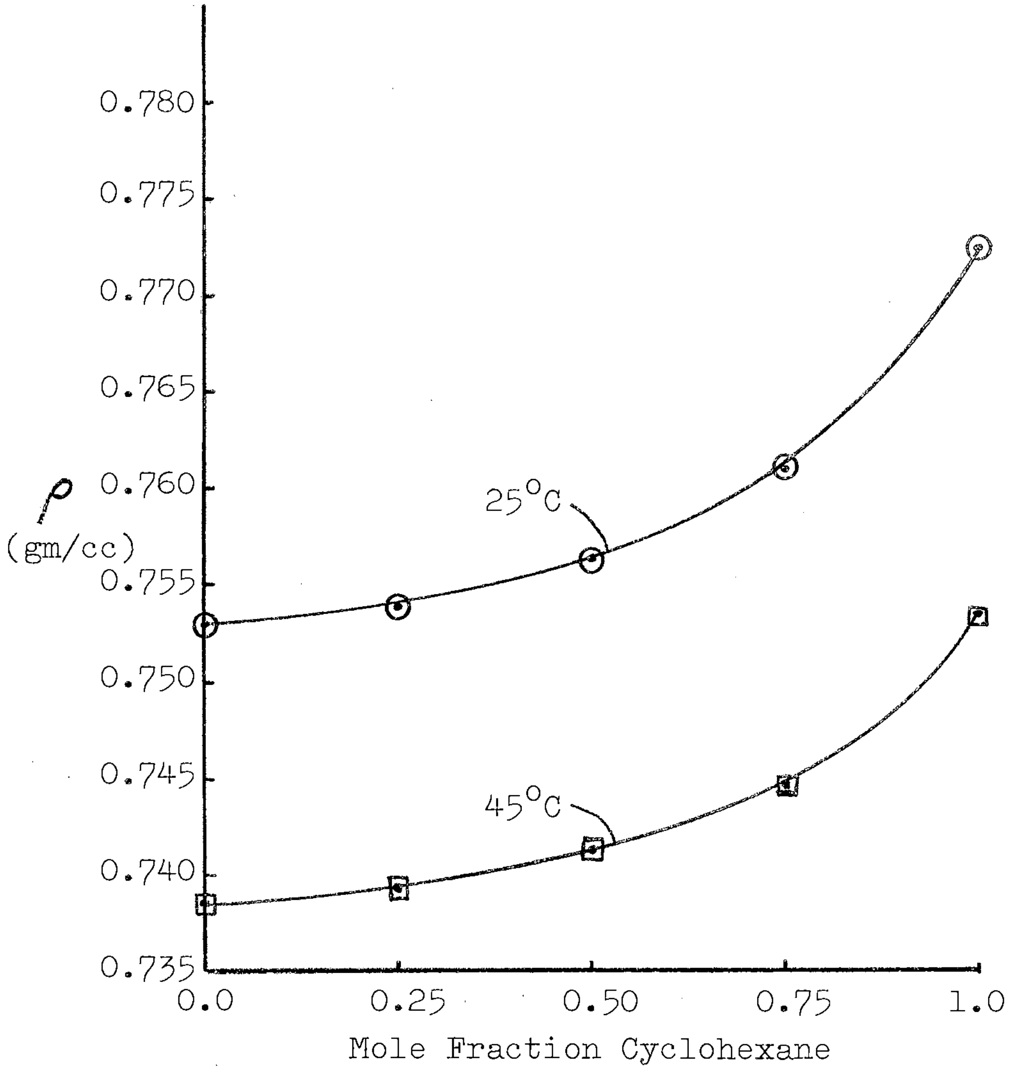

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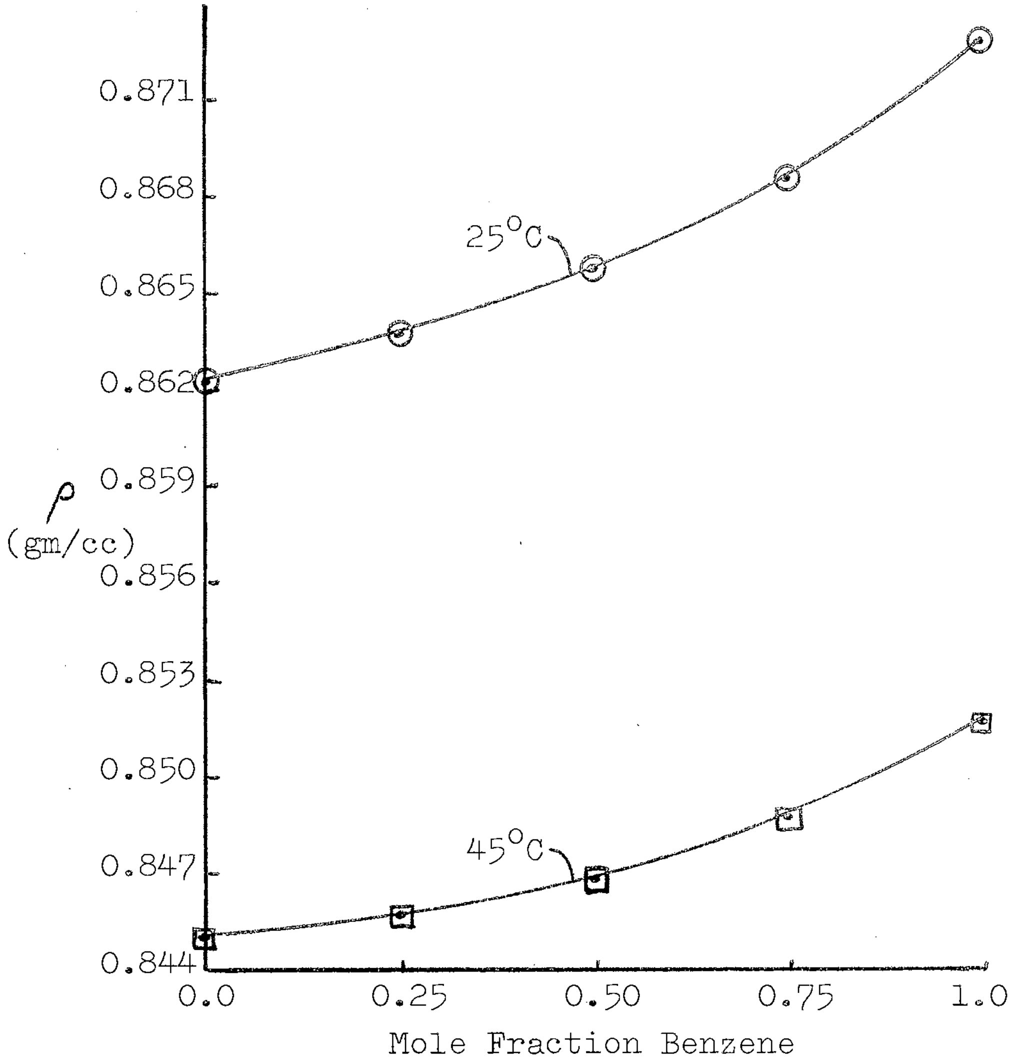
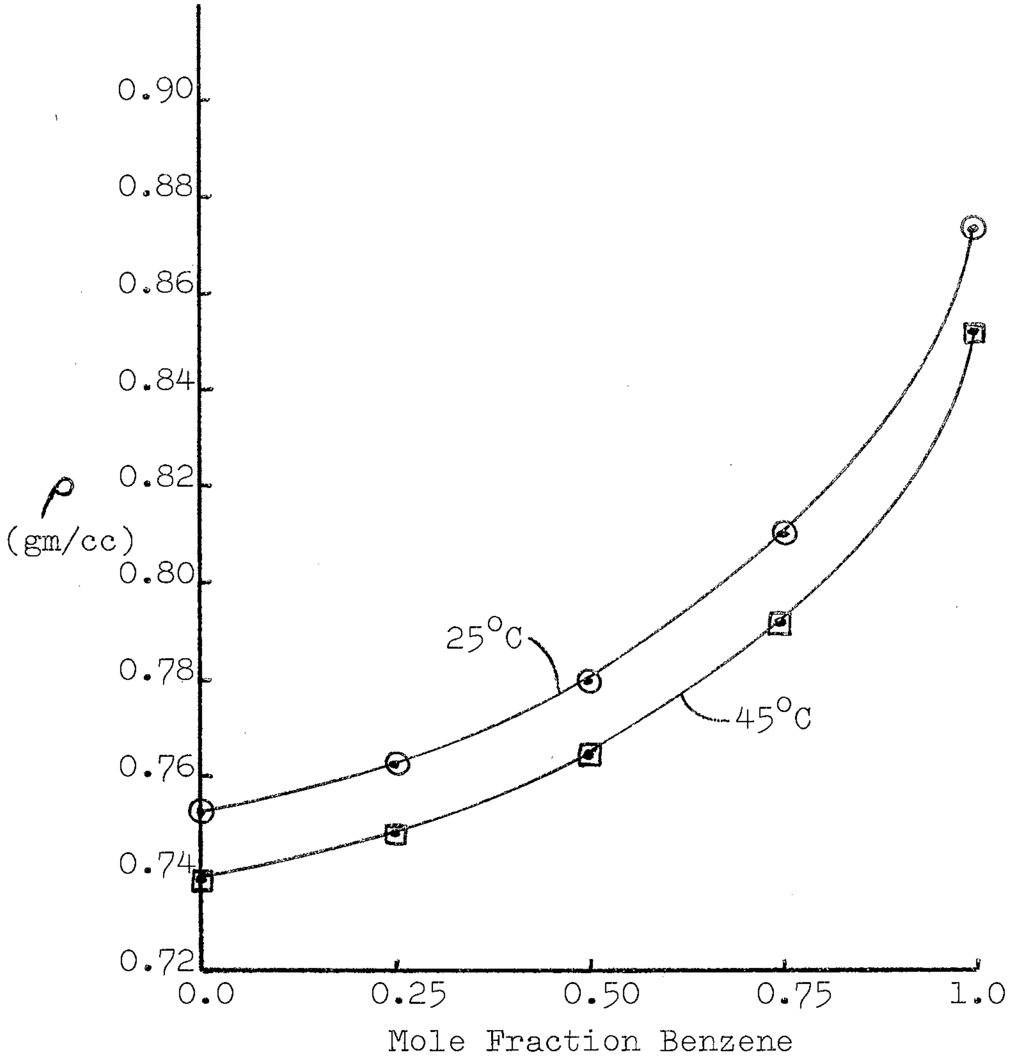


Figure 16. Effect of Composition on Density for the Benzene—Ethylbenzene Binary System



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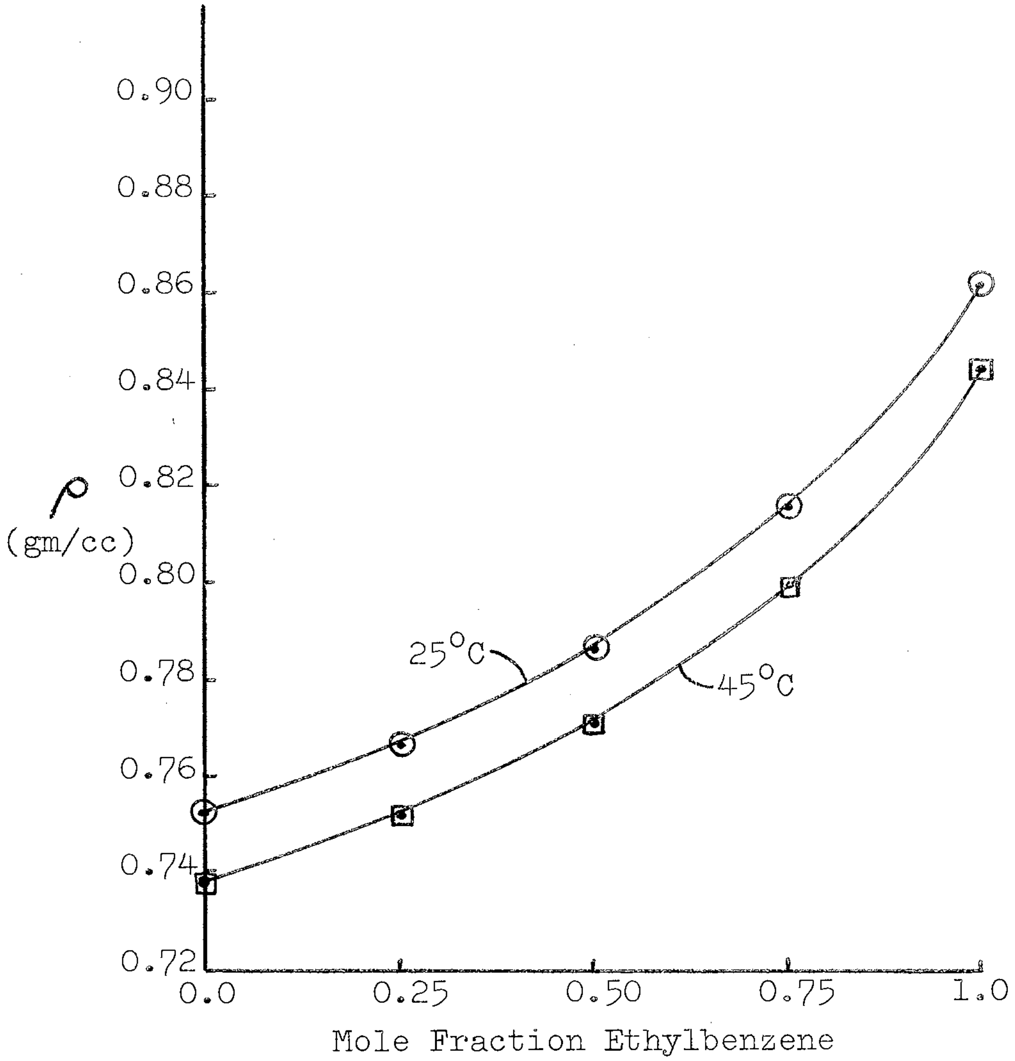


Figure 18. Effect of Composition on Density for the Ethylbenzene—n-Tridecane Binary System

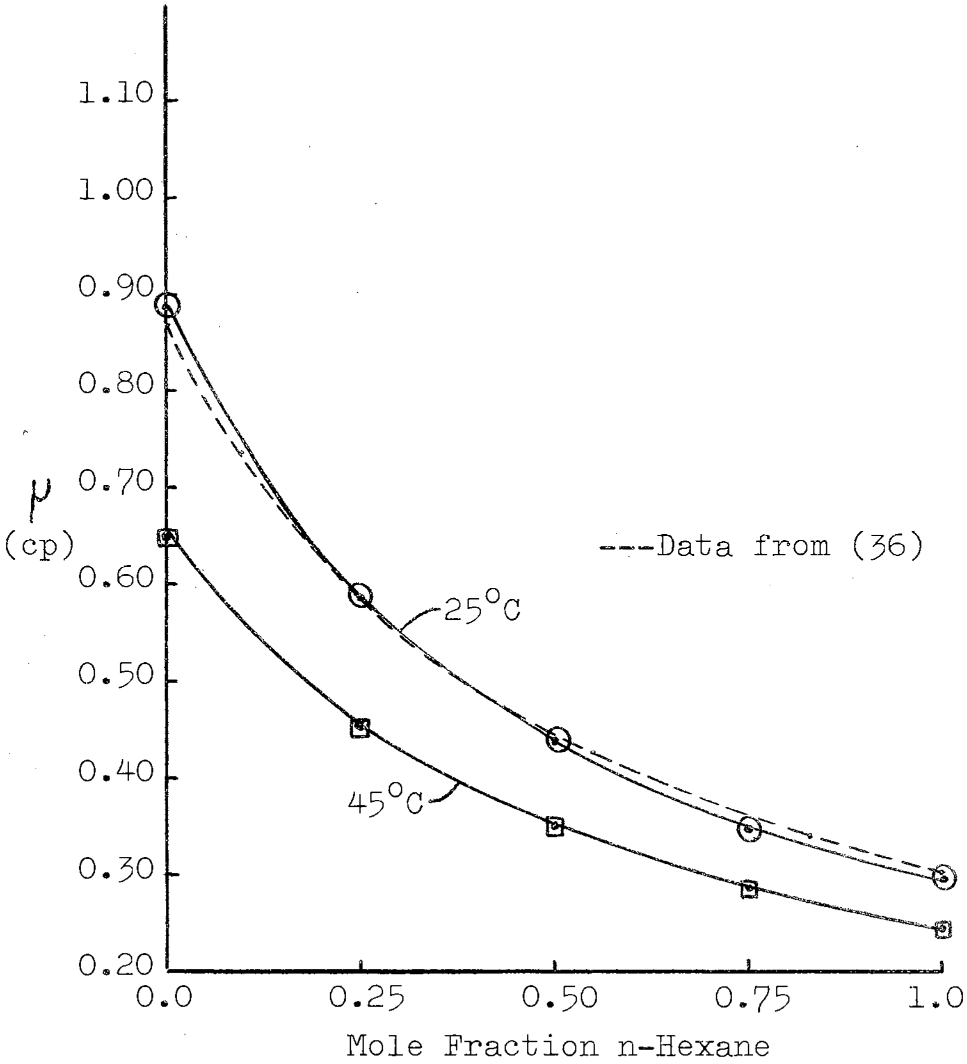


Figure 19. Effect of Composition on Viscosity for the n-Hexane—Cyclohexane Binary System

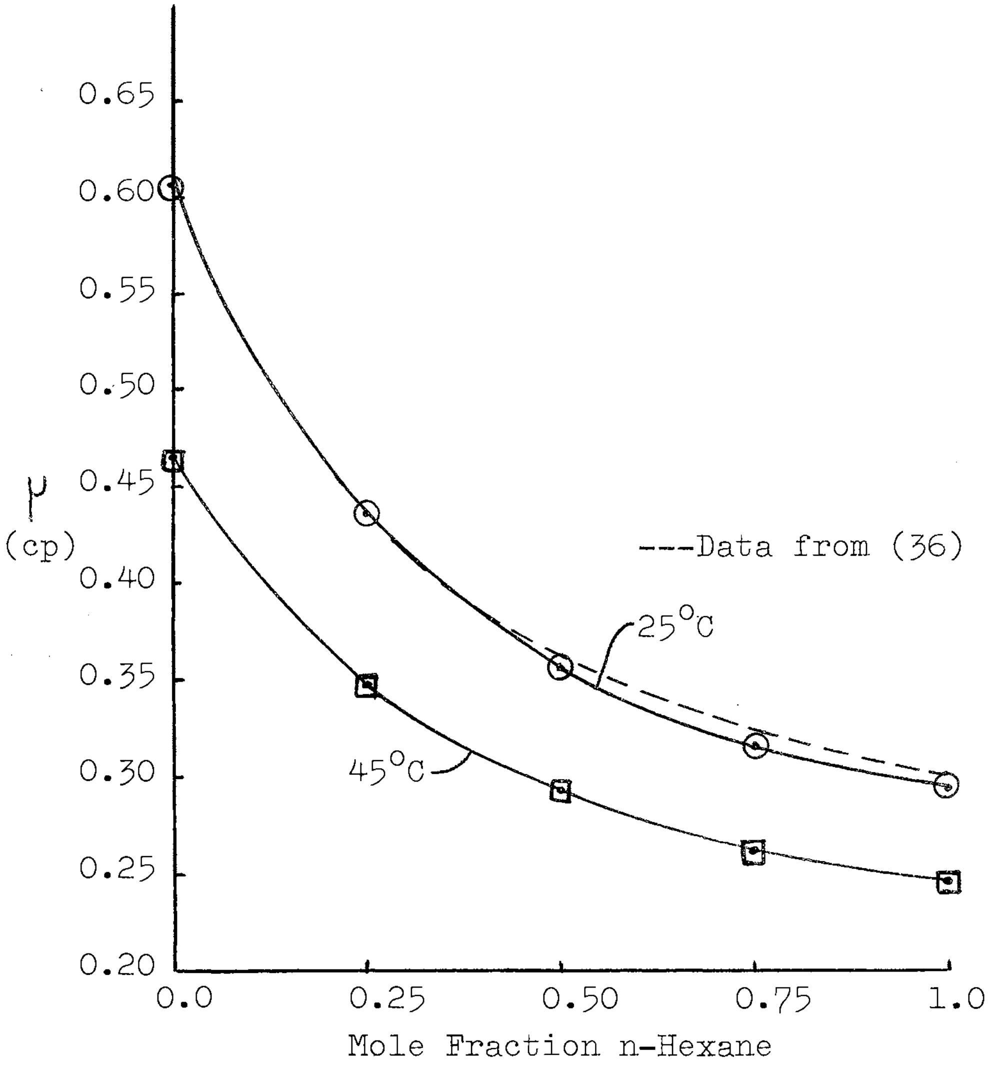


Figure 20. Effect of Composition on Viscosity for the n-Hexane—Benzene Binary System

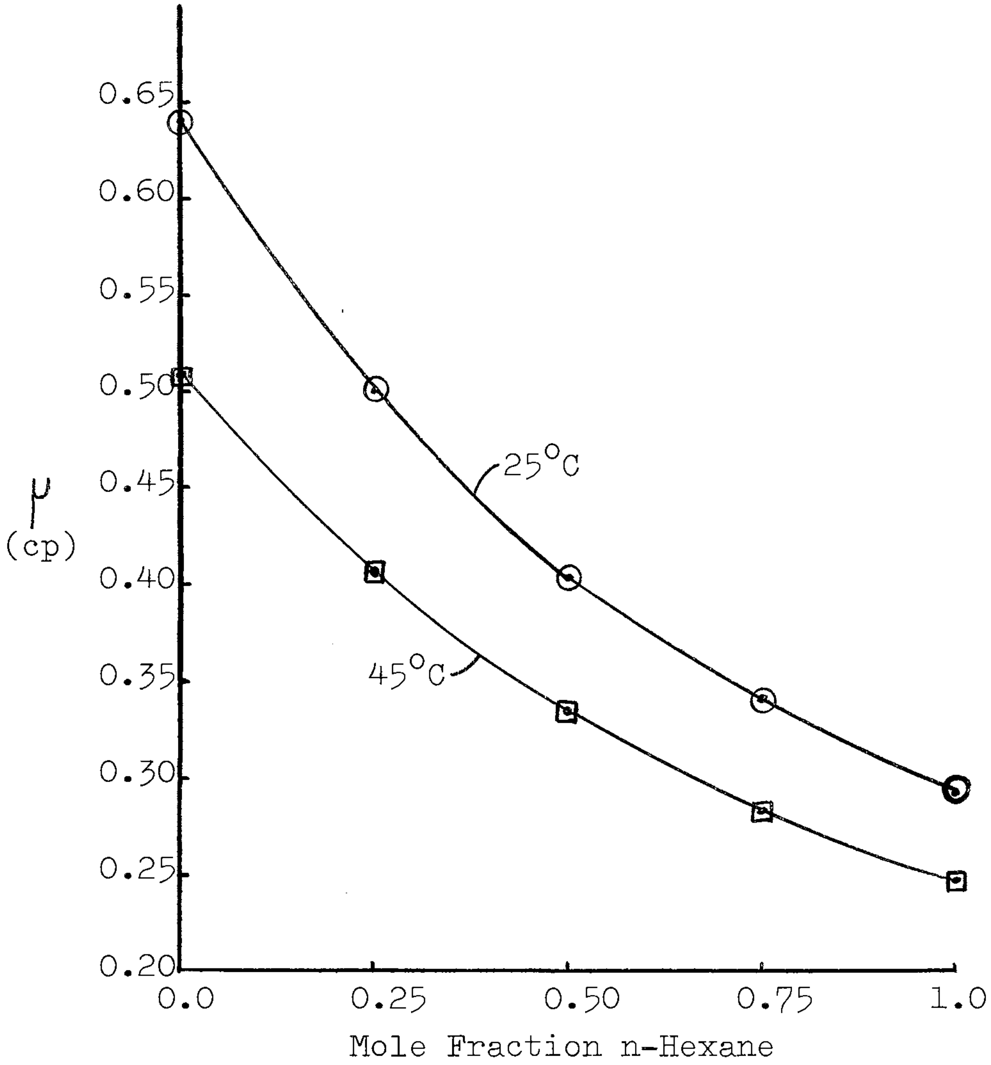


Figure 21. Effect of Composition on Viscosity for the n-Hexane—Ethylbenzene Binary System

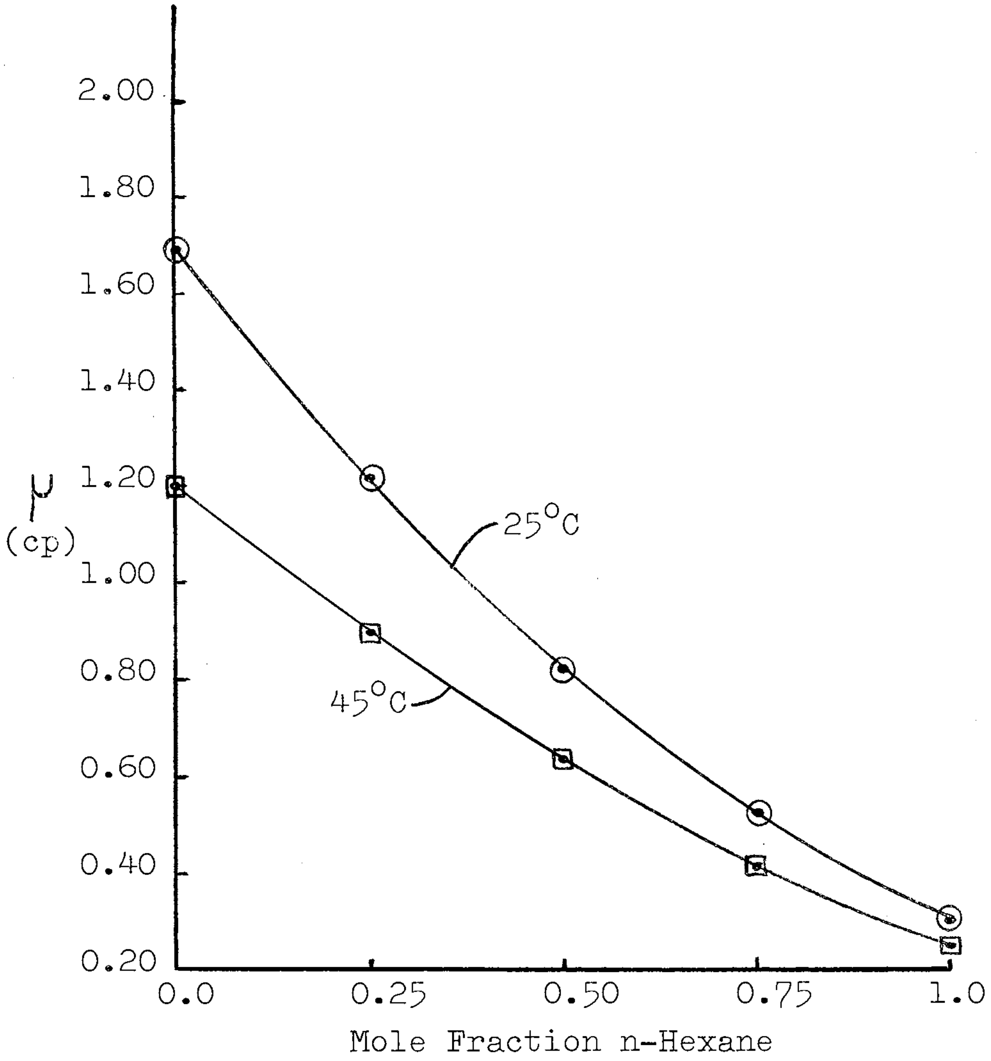
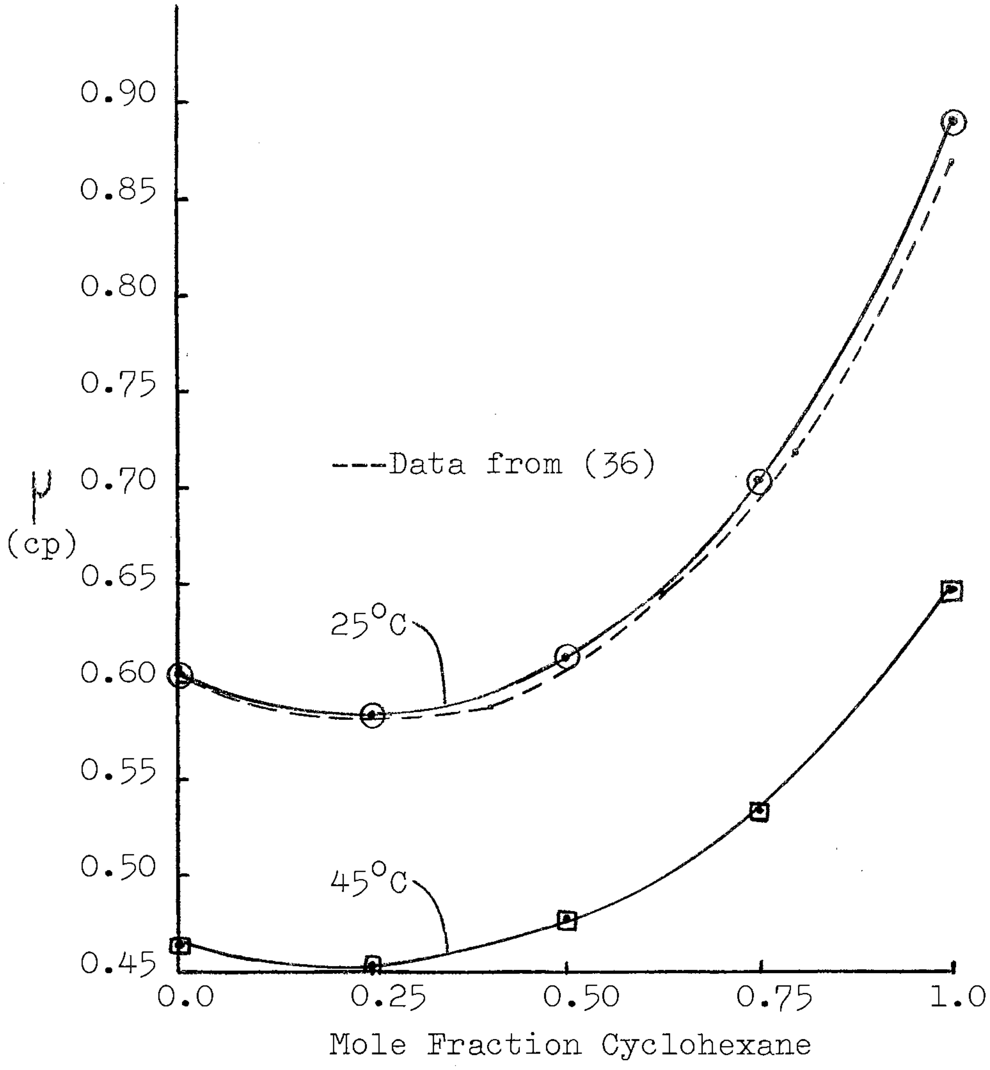


Figure 22. Effect of Composition on Viscosity for the n-Hexane—n-Tridecane Binary System



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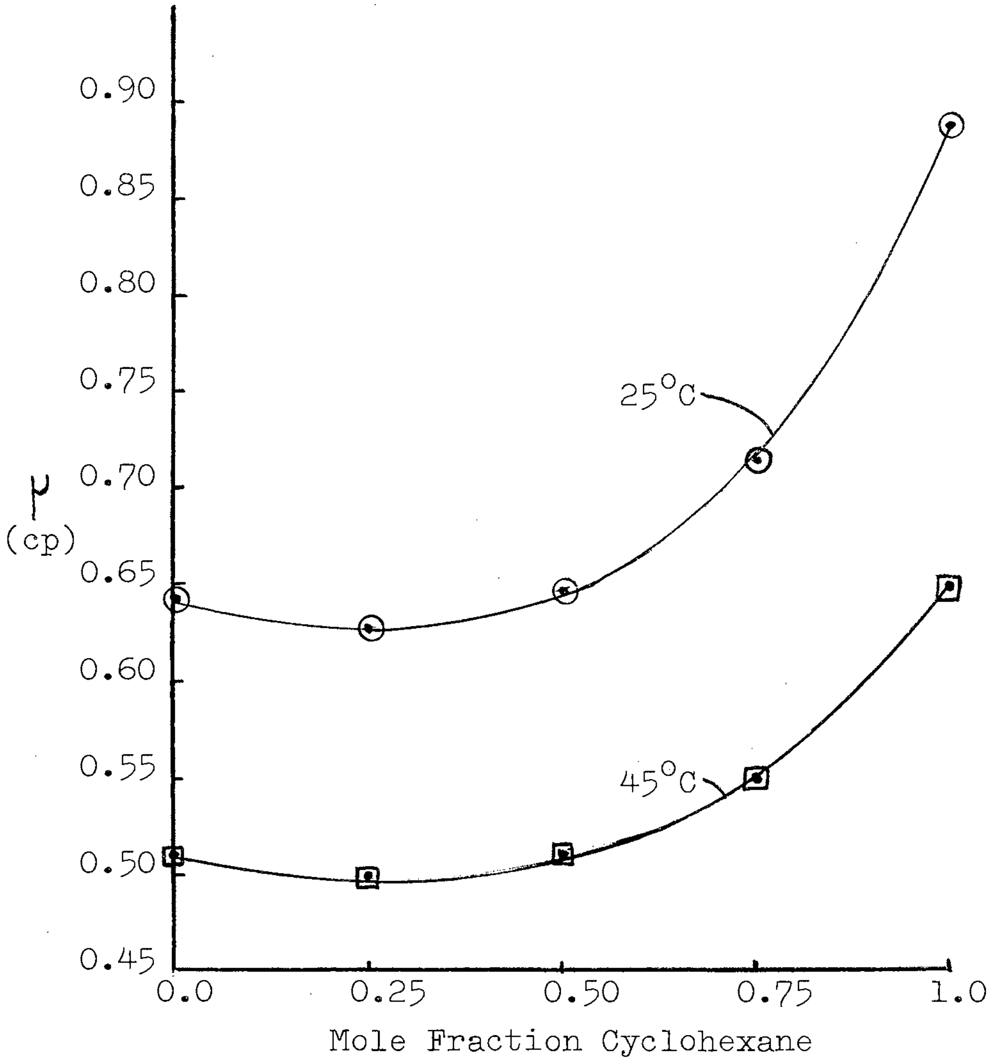

Figure 24. Effect of Composition on Viscosity for the Cyclohexane—Ethylbenzene Binary System

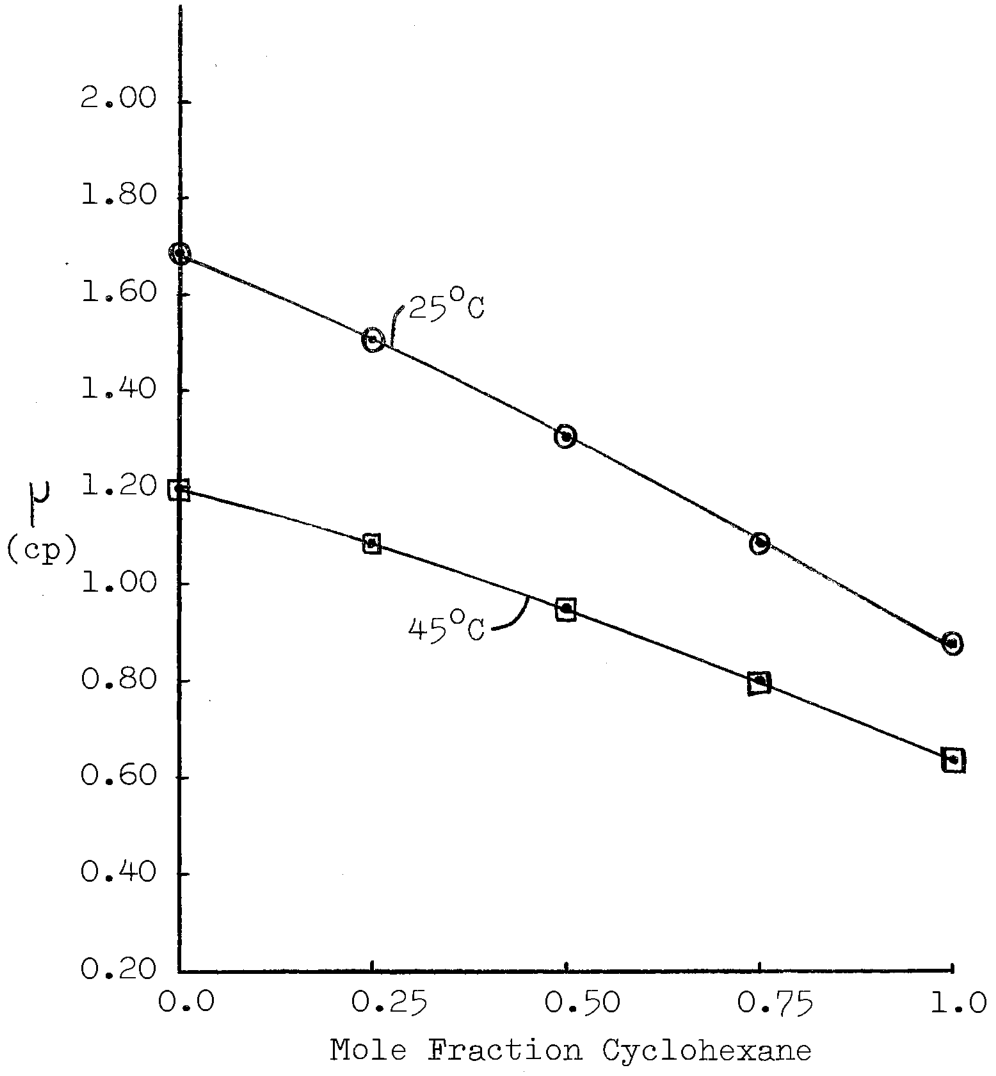

Figure 25. Effect of Composition on Viscosity for the Cyclohexane—n-Tridecane Binary System

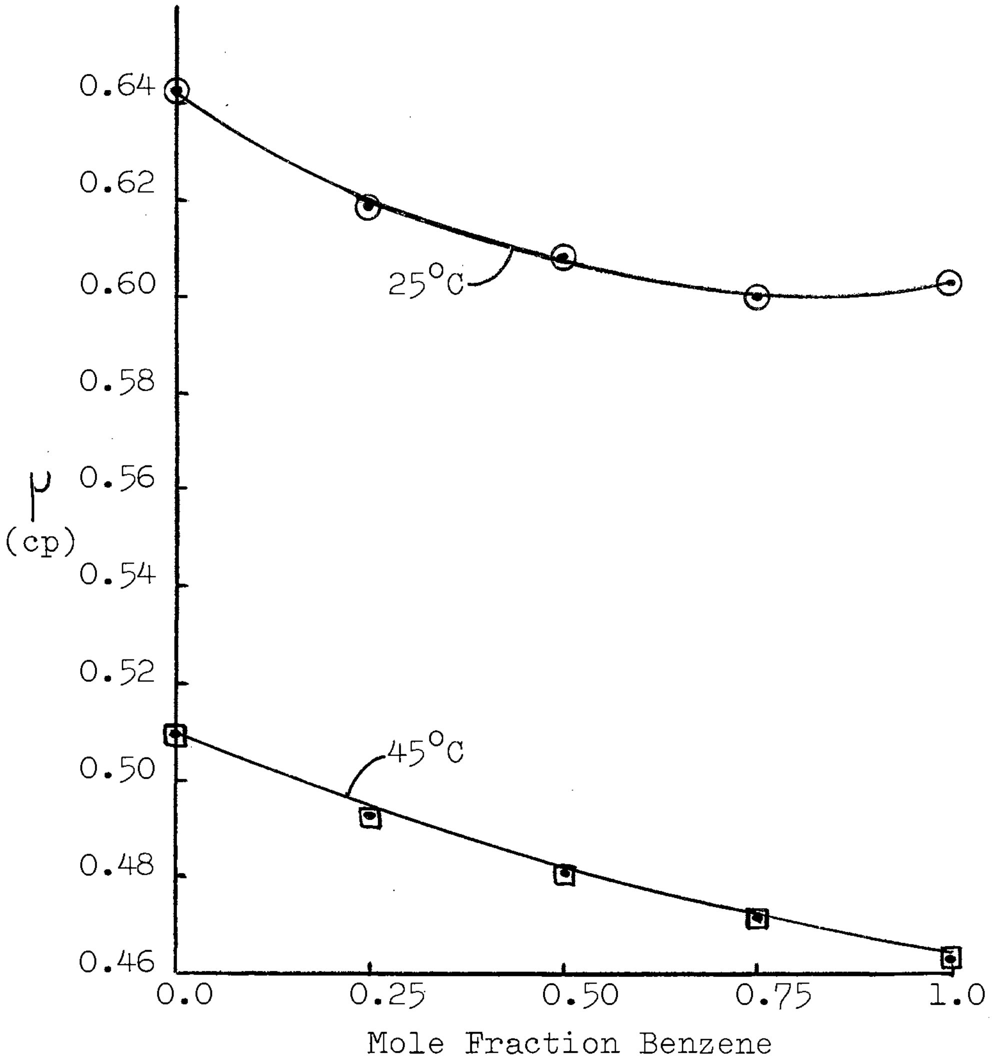

Figure 26. Effect of Composition on Viscosity for the Benzene—Ethylbenzene Binary System

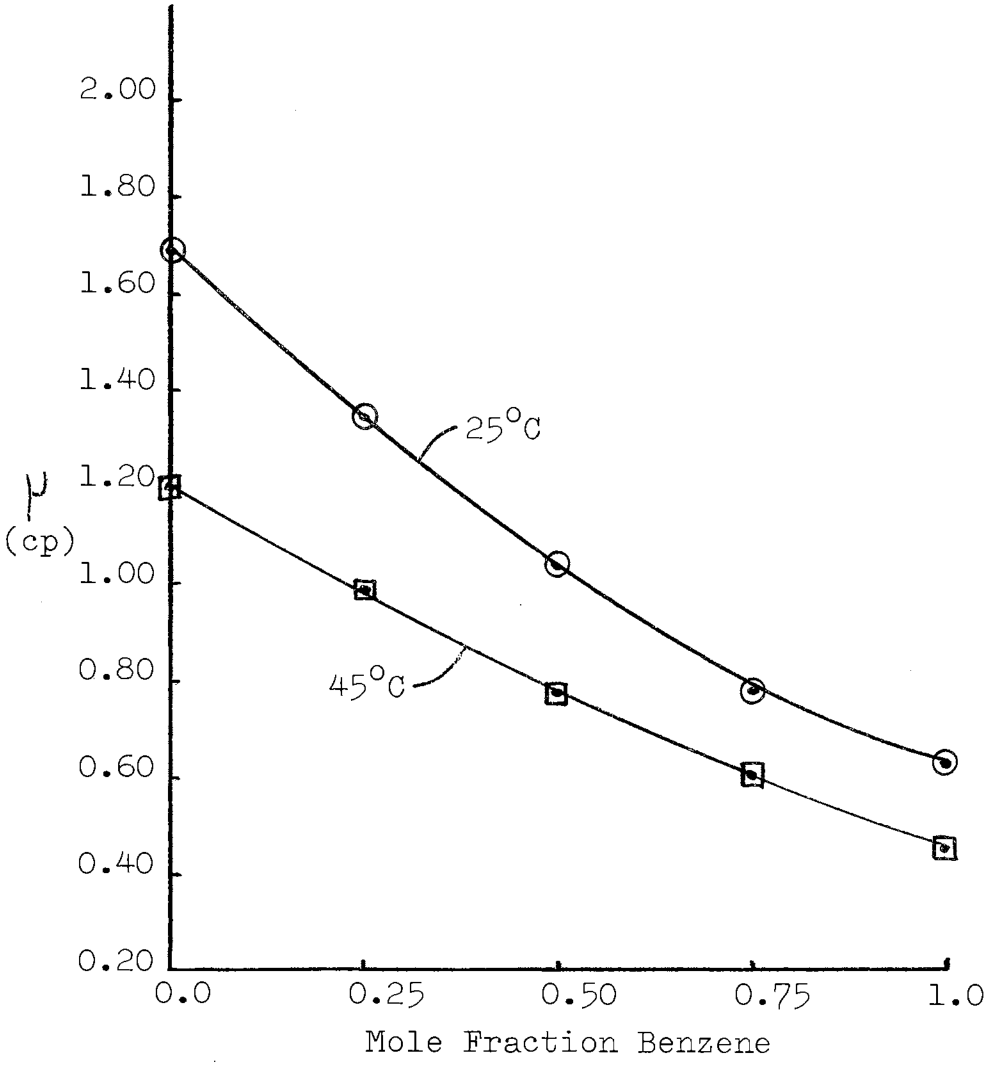

Figure 27. Effect of Composition on Viscosity for the Benzene—n-Tridecane Binary System

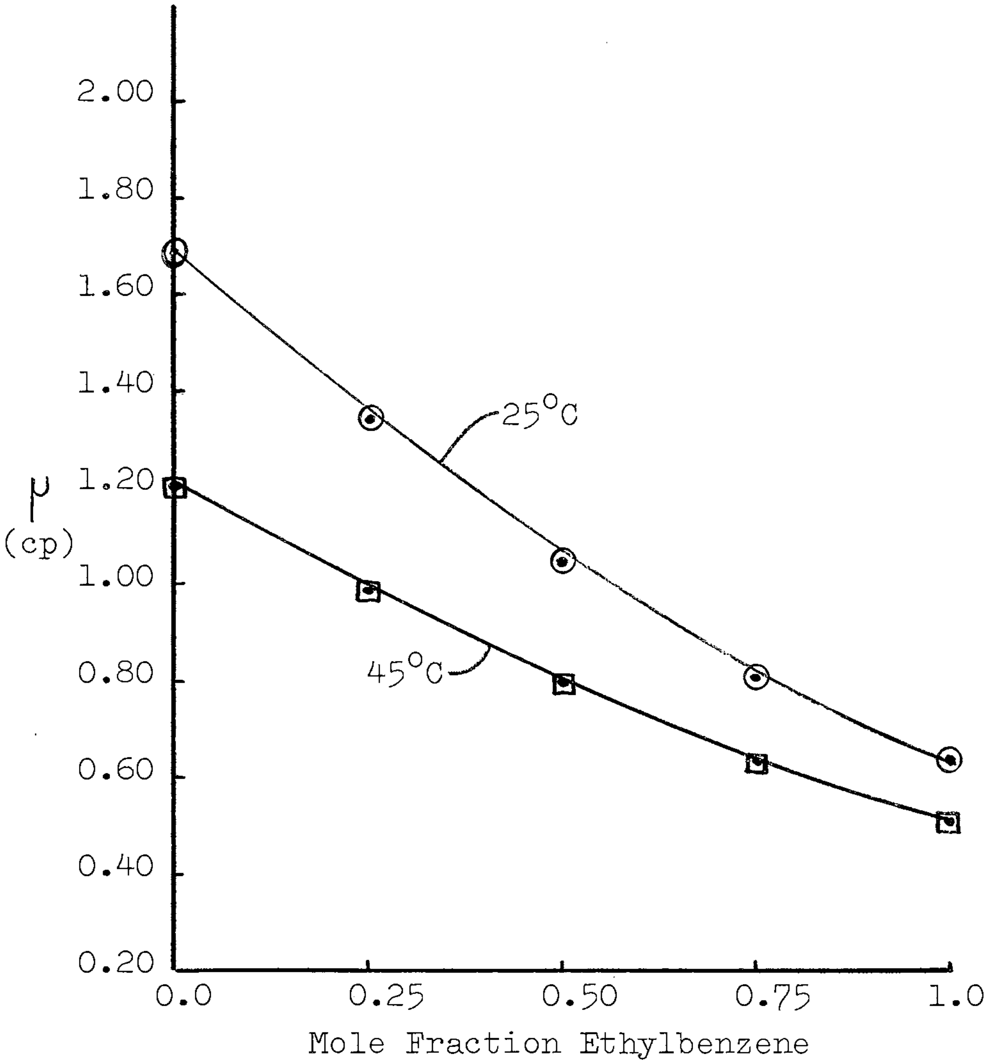

Figure 28. Effect of Composition on Viscosity for the Ethylbenzene—n-Tridecane Binary System

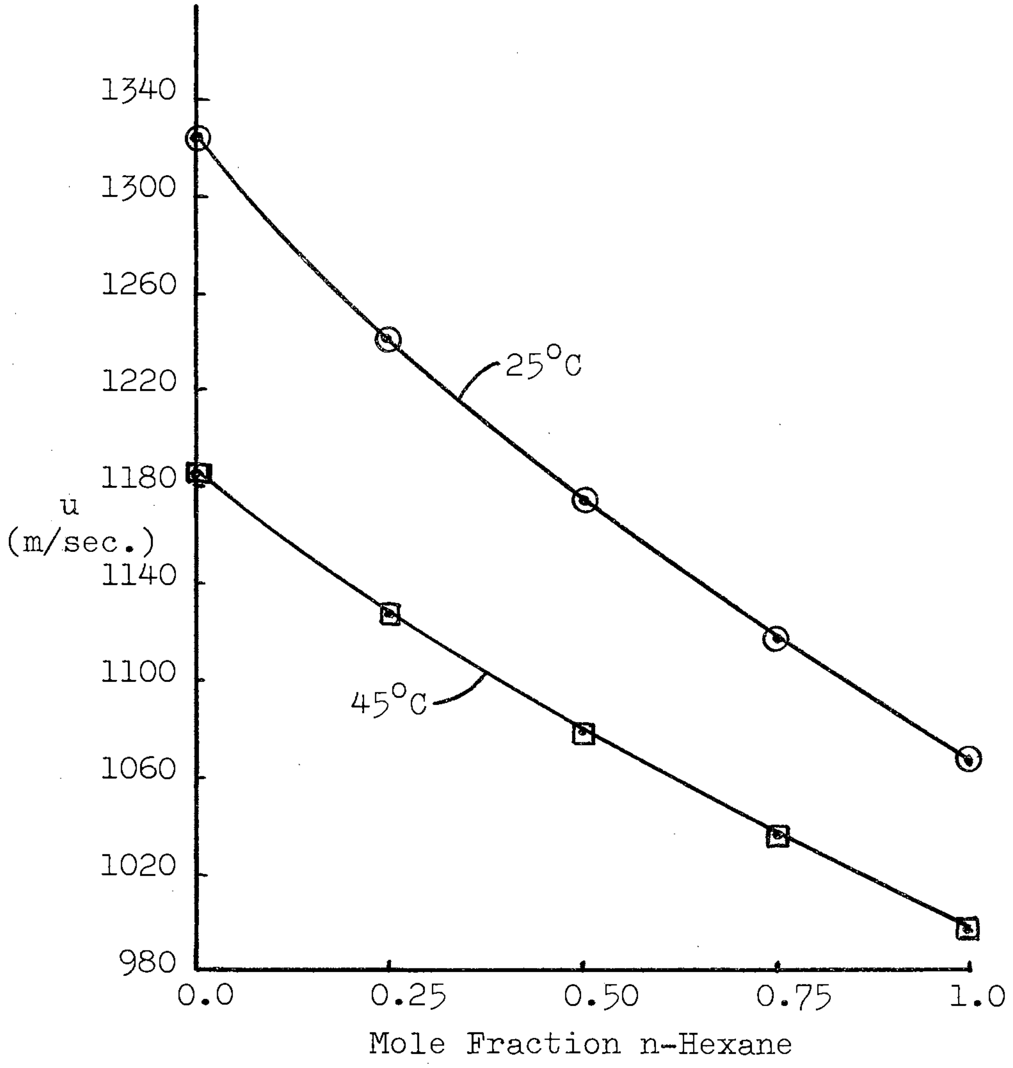

Figure 29. Effect of Composition on Ultrasonic Velocity for the n-Hexane—Cyclohexane Binary System

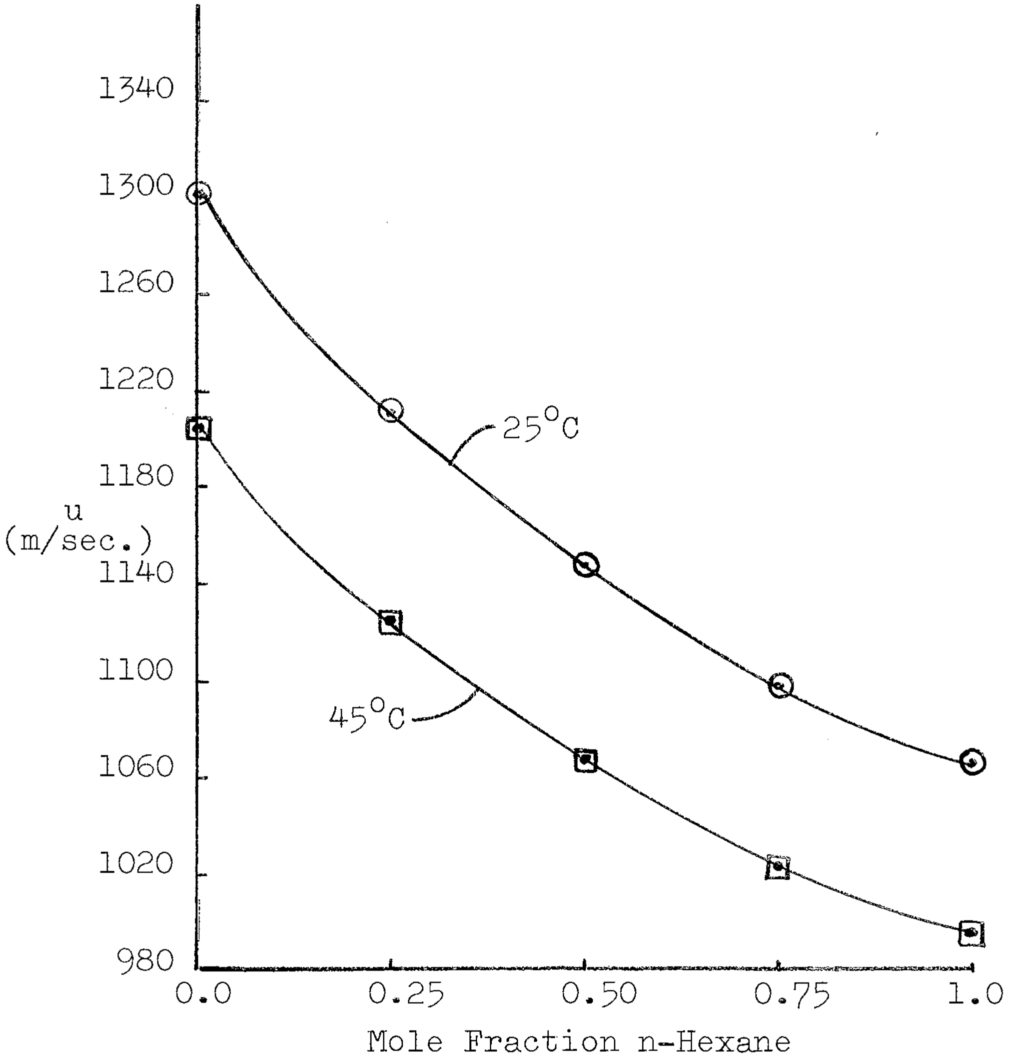

Figure 30. Effect of Composition on Ultrasonic Velocity for the n-Hexane—Benzene Binary System

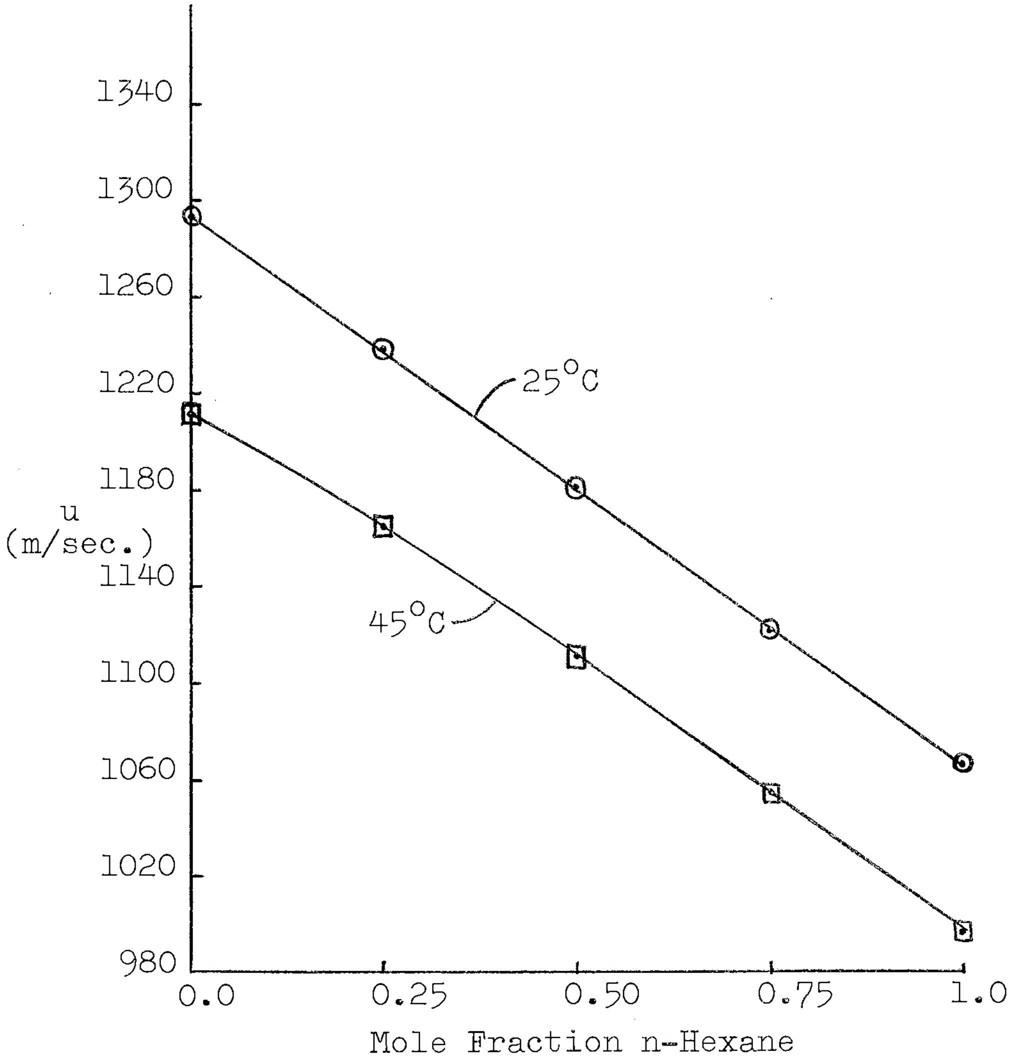

Figure 31. Effect of Composition on Ultrasonic Velocity for the n-Hexane—Ethylbenzene Binary System

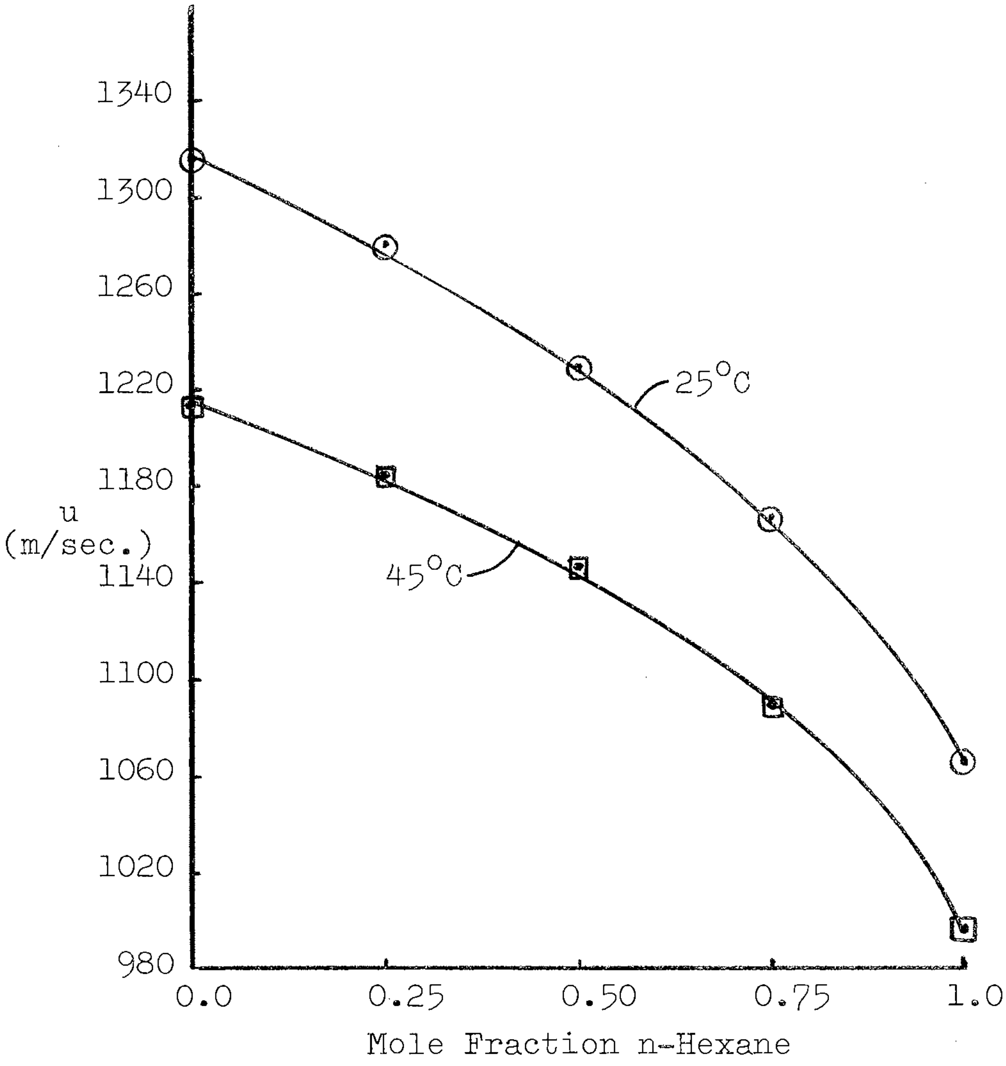

Figure 32. Effect of Composition on Ultrasonic Velocity for the n-Hexane—n-Tridecane Binary System

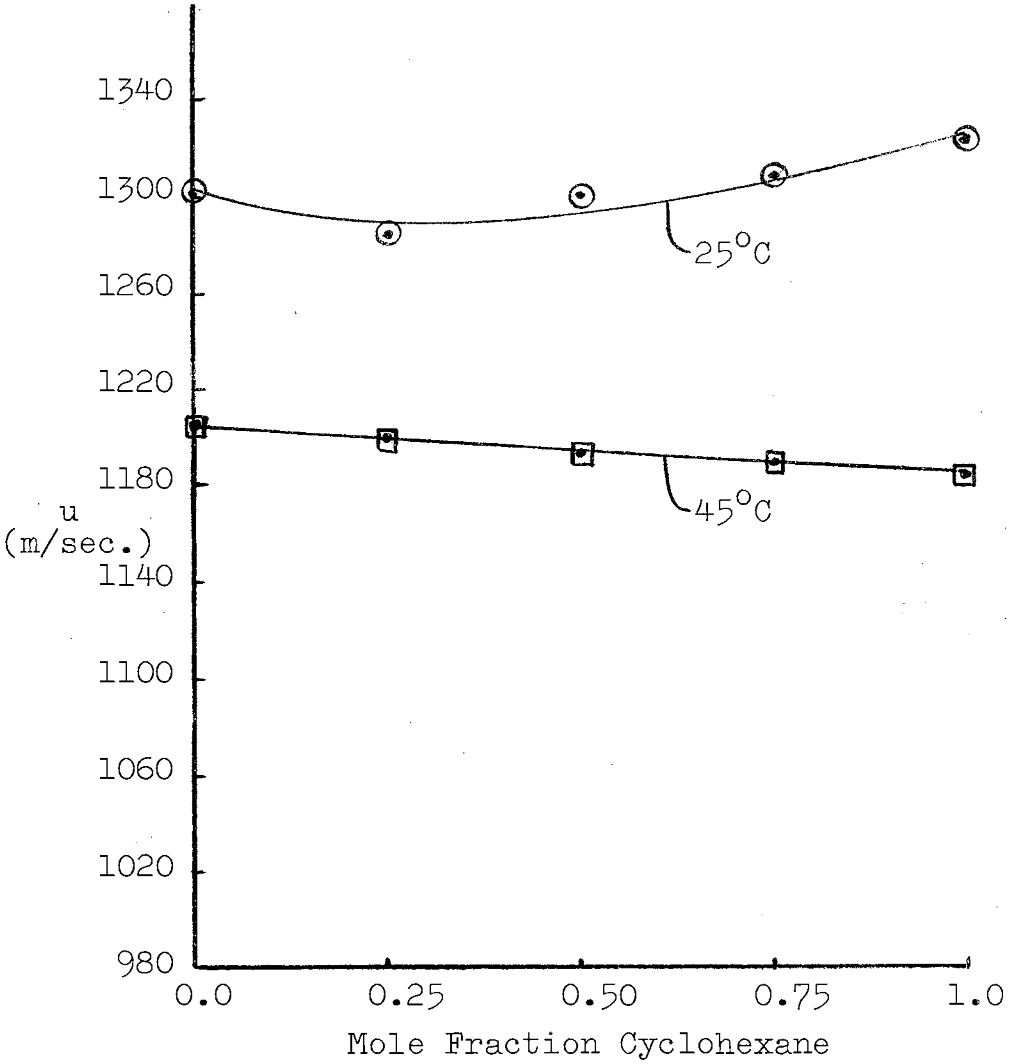

Figure 33. Effect of Composition on Ultrasonic Velocity for the Cyclohexane— Benzene Binary System

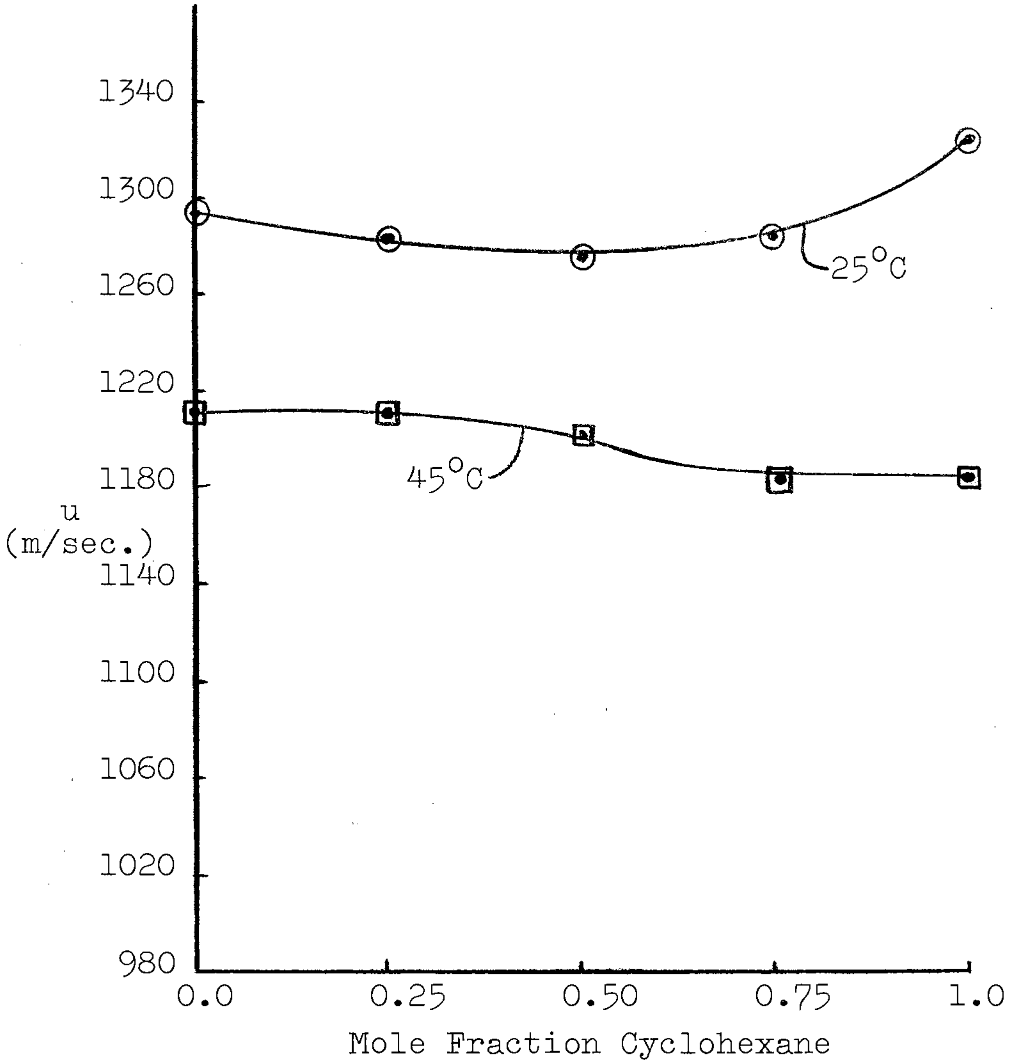

Figure 34. Effect of Composition on Ultrasonic Velocity for the Cyclohexane—Ethylbenzene Binary System

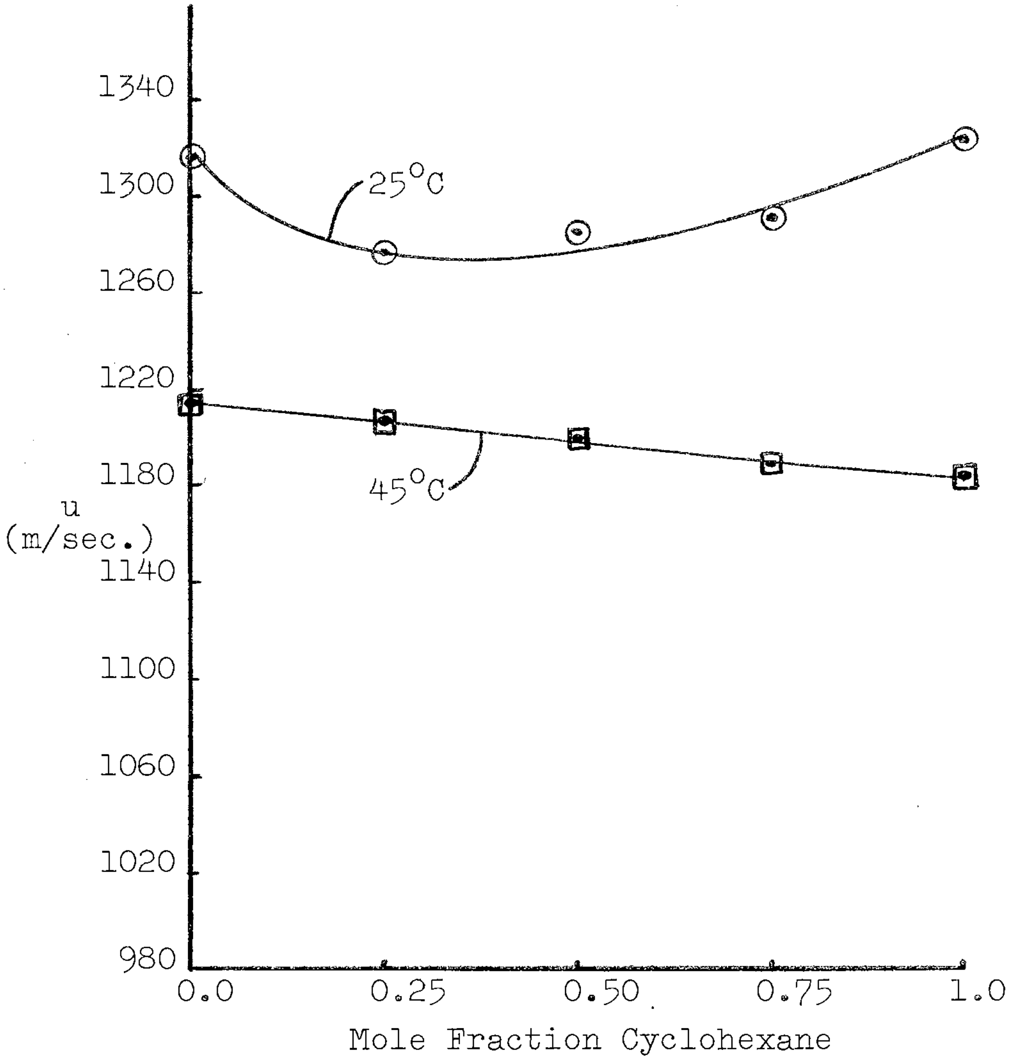

Figure 35. Effect of Composition on Ultrasonic Velocity for the Cyclohexane—n-Tridecane Binary System

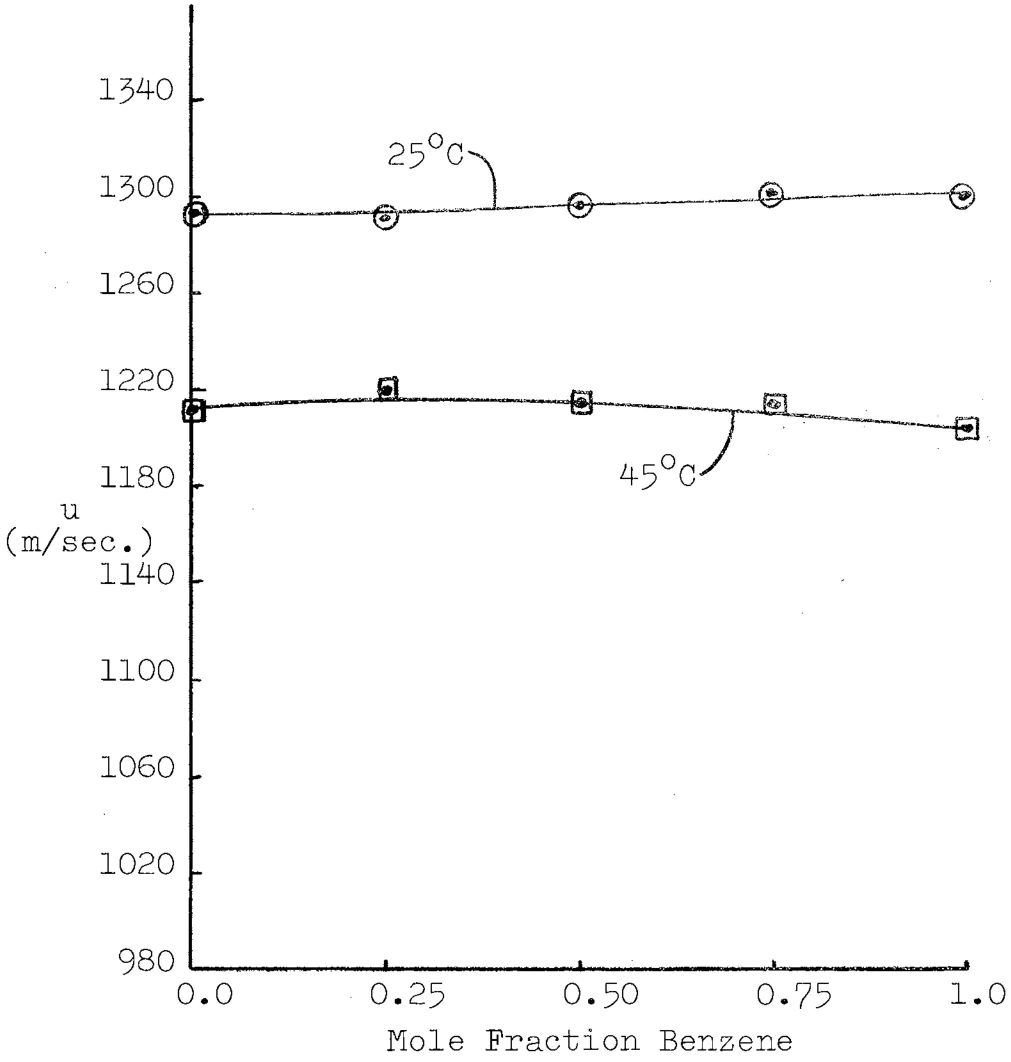

Figure 36. Effect of Composition on Ultrasonic Velocity for the Benzene—Ethylbenzene Binary System

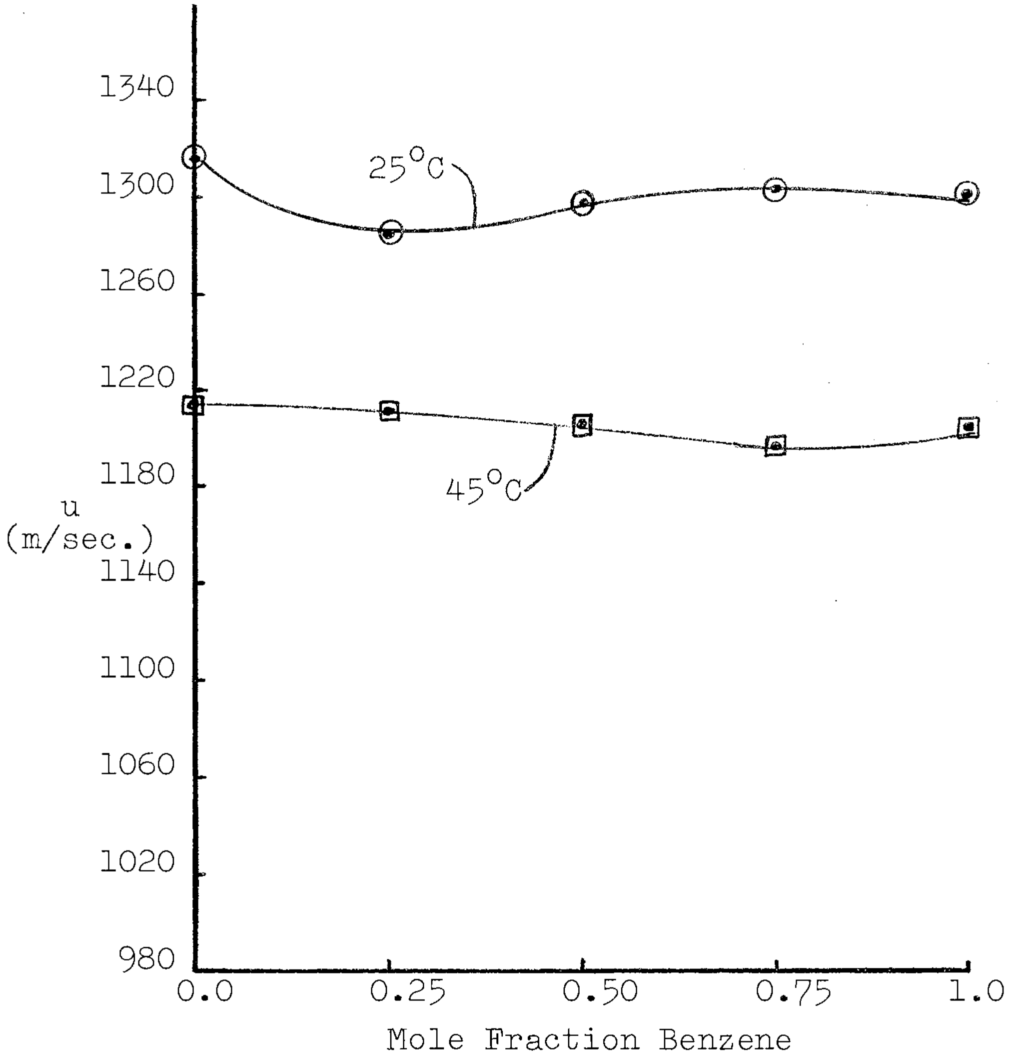

Figure 37. Effect of Composition on Ultrasonic Velocity for the Benzene—n-Tridecane Binary System

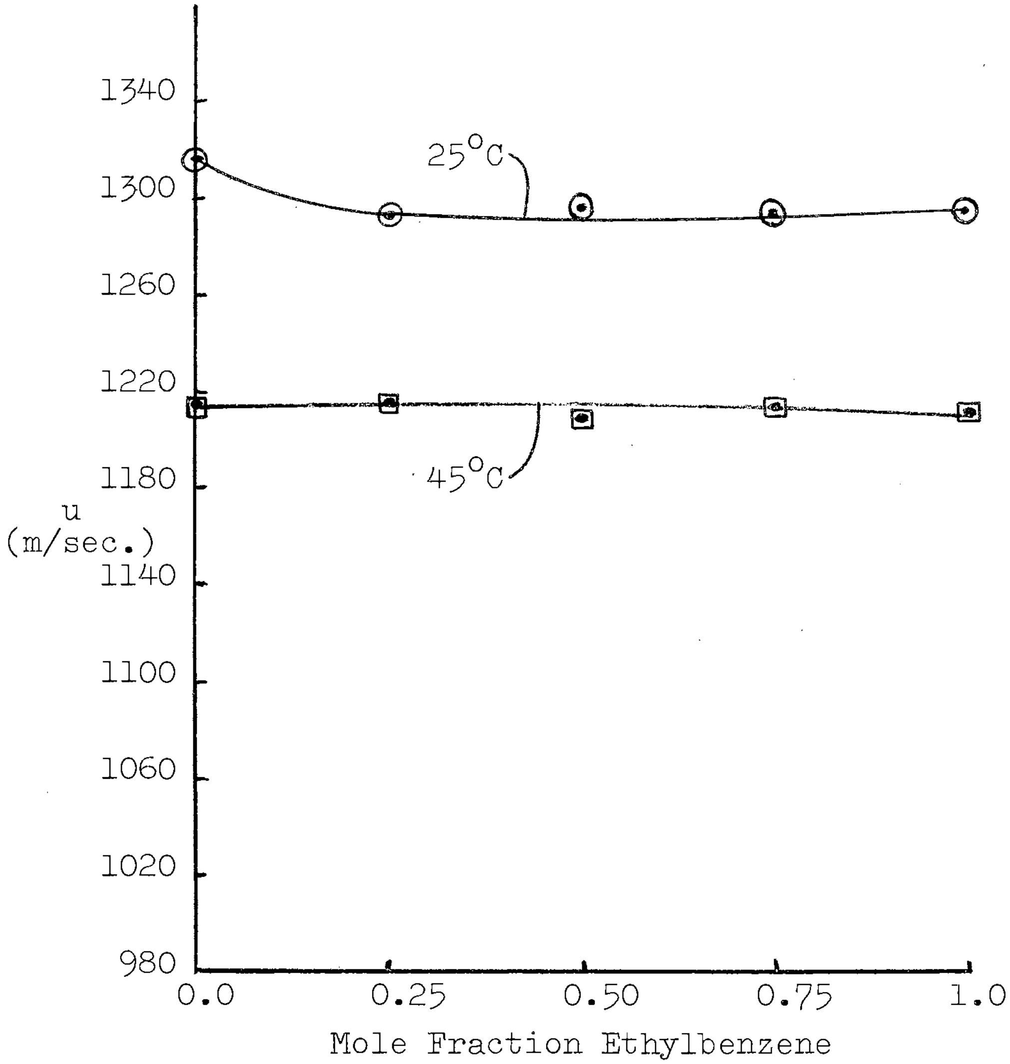

Figure 38. Effect of Composition on Ultrasonic Velocity for the Ethylbenzene—n-Tridecane Binary System

TABLE II

EXPERIMENTAL LIQUID COMPOSITIONS

Ident. Number	Composition (Mole Fraction)				
	n-Hexane	Cyclohexane	Benzene	Ethylbenzene	n-Tridecane
I	1.0000	--	--	--	--
II	--	1.0000	--	--	--
III	--	--	1.0000	--	--
IV	--	--	--	1.0000	--
V	--	--	--	--	1.0000
1	0.2502	0.7498	--	--	--
2	0.5008	0.4992	--	--	--
3	0.7500	0.2500	--	--	--
4	0.2500	--	0.7500	--	--
5	0.5000	--	0.5000	--	--
6	0.7500	--	0.2500	--	--
7	0.2500	--	--	0.7500	--
8	0.5000	--	--	0.5000	--
9	0.7500	--	--	0.2500	--
10	0.2500	--	--	--	0.7500
11	0.5000	--	--	--	0.5000
12	0.7500	--	--	--	0.2500
13	--	0.2500	0.7500	--	--
14	--	0.5000	0.5000	--	--
15	--	0.7500	0.2500	--	--
16	--	0.2500	--	0.7500	--
17	--	0.5000	--	0.5000	--
18	--	0.7500	--	0.2500	--
19	--	0.2500	--	--	0.7500
20	--	0.5000	--	--	0.5000
21	--	0.7500	--	--	0.2500
22	--	--	0.2500	0.7500	--
23	--	--	0.5000	0.5000	--
24	--	--	0.7500	0.2500	--
25	--	--	0.2500	--	0.7500
26	--	--	0.5000	--	0.5000
27	--	--	0.7500	--	0.2500
28	--	--	--	0.2500	0.7500
29	--	--	--	0.5000	0.5000
30	--	--	--	0.7500	0.2500
31	0.5000	0.2500	--	0.2500	--
32	0.2500	0.5000	--	0.2500	--
33	0.2500	0.2500	--	0.5000	--
34	0.5000	0.2500	--	--	0.2500
35	0.2500	0.5000	--	--	0.2500
36	0.2500	0.2500	--	--	0.5000

TABLE II (Continued)

Ident. Number	Composition (Mole Fraction)				
	n-Hexane	Cyclo-hexane	Benzene	Ethyl-benzene	n-Tri-decane
37	0.5000	--	--	0.2500	0.2500
38	0.2500	--	--	0.5000	0.2500
39	0.2500	--	--	0.2500	0.5000
40	--	0.5000	--	0.2500	0.2500
41	--	0.2500	--	0.5000	0.2500
42	--	0.2500	--	0.2500	0.5000
43	--	0.2500	0.5000	0.2500	--
44	0.4000	0.2000	--	0.2000	0.2000
45	0.2000	0.4000	--	0.2000	0.2000
46	0.2000	0.2000	--	0.4000	0.2000
47	0.2000	0.2000	--	0.2000	0.4000

TABLE III

EXPERIMENTAL DENSITY DATA

Ident. Number	Density (gm/cc)		Ident. Number	Density (gm/cc)	
	T = 25°C	T = 45°C		T = 25°C	T = 45°C
I	0.6548	0.6363	22	0.8638	0.8458
II	0.7725	0.7535	23	0.8658	0.8469
III	0.8729	0.8517	24	0.8686	0.8487
IV	0.8623	0.8450	25	0.7634	0.7488
V	0.7528	0.7385	26	0.7802	0.7646
1	0.7381	0.7196	27	0.8096	0.7919
2	0.7076	0.6892	28	0.7672	0.7526
3	0.6800	0.6617	29	0.7874	0.7721
4	0.7991	0.7793	30	0.8164	0.8002
5	0.7407	0.7214	31	0.7321	0.7146
6	0.6934	0.6745	32	0.7616	0.7436
7	0.8093	0.7926	33	0.7855	0.7678
8	0.7568	0.7397	34	0.7149	0.6988
9	0.7049	0.6872	35	0.7371	0.7210
10	0.7388	0.7244	36	0.7377	0.7229
11	0.7203	0.7053	37	0.7341	0.7183
12	0.6942	0.6780	38	0.7750	0.7591
13	0.8398	0.8195	39	0.7535	0.7384
14	0.8126	0.7925	40	0.7795	0.7633
15	0.7903	0.7707	41	0.7982	0.7820
16	0.8401	0.8226	42	0.7719	0.7567
17	0.8169	0.7990	43	0.8392	0.8201
18	0.7940	0.7759	44	0.7387	0.7223
19	0.7538	0.7394	45	0.7578	0.7415
20	0.7563	0.7412	46	0.7736	0.7574
21	0.7610	0.7447	47	0.7549	0.7395

TABLE IV

EXPERIMENTAL VISCOSITY DATA

Ident. Number	Viscosity (cp)		Ident. Number	Viscosity (cp)	
	T = 25°C	T = 45°C		T = 25°C	T = 45°C
I	0.2954	0.2453	22	0.6194	0.4928
II	0.8884	0.6484	23	0.6080	0.4808
III	0.6025	0.4632	24	0.5995	0.4717
IV	0.6416	0.5100	25	1.3504	0.9912
V	1.6940	1.1970	26	1.0397	0.7904
1	0.5866	0.4580	27	0.7838	0.6081
2	0.4398	0.3542	28	1.3434	0.9894
3	0.3535	0.2886	29	1.0493	0.8005
4	0.4346	0.3493	30	0.8148	0.6384
5	0.3564	0.2932	31	0.4156	0.3395
6	0.3149	0.2620	32	0.5279	0.4177
7	0.5006	0.4073	33	0.5022	0.4061
8	0.4070	0.3360	34	0.6408	0.5053
9	0.3412	0.2833	35	0.8127	0.6226
10	1.2186	0.9004	36	1.0272	0.7713
11	0.8330	0.6427	37	0.5988	0.4786
12	0.5269	0.4214	38	0.6901	0.5489
13	0.5821	0.4506	39	0.9321	0.7148
14	0.6143	0.4760	40	0.9363	0.7116
15	0.7037	0.5342	41	0.8586	0.6636
16	0.6276	0.4990	42	1.1486	0.8614
17	0.6493	0.5109	43	0.5968	0.4680
18	0.7141	0.5495	44	0.6136	0.4899
19	1.5136	1.0870	45	0.7382	0.5761
20	1.3085	0.9523	46	0.6947	0.5499
21	1.0937	0.8055	47	0.9023	0.6938

TABLE V

EXPERIMENTAL ULTRASONIC VELOCITY DATA

Ident. Number	Ultrasonic Velocity (m/sec.)		Ident. Number	Ultrasonic Velocity (m/sec.)	
	T = 25°C	T = 45°C		T = 25°C	T = 45°C
I	1067	997	22	1292	1220
II	1324	1184	23	1297	1214
III	1301	1205	24	1303	1214
IV	1294	1212	25	1285	1211
V	1316	1214	26	1298	1205
1	1242*	1128*	27	1304	1196
2	1174*	1080*	28	1293	1216
3	1118*	1036*	29	1295	1208
4	1211*	1125*	30	1294	1213
5	1148*	1068*	31	1295	1166
6	1099*	1024*	32	1315	1182
7	1239*	1164*	33	1304	1190
8	1181*	1112*	34	1323	1180
9	1122*	1055*	35	1324	1192
10	1281*	1184*	36	1316	1185
11	1229*	1148*	37	1318	1187
12	1168*	1090*	38	1302	1190
13	1285	1199	39	1305	1193
14	1301	1193	40	1300	1198
15	1309	1190	41	1300	1209
16	1284	1210	42	1301	1211
17	1276	1202	43	1296	1207
18	1283	1184	44	1326	1187
19	1278	1208	45	1320	1194
20	1285	1201	46	1318	1185
21	1292	1189	47	1305	1187

*Adjusted values. See CHAPTER IV, pages 53 and 54.

TABLE VI

VALUES OF FLUIDITY CALCULATED WITH PROPOSED CORRELATION (EQUATION (27)) COMPARED TO EXPERIMENTAL VALUES AT 25°C

	Fluidity (cp^{-1})		
Ident. Number	Exp.	Calc.	% Dev.
I	3.385	3.385	0.00
II	1.126	1.453	-29.04
III	1.660	2.050	-23.49
IV	1.559	1.285	17.58
V	0.590	0.560	5.08
1	1.705	1.902	-11.55
2	2.274	2.381	- 4.71
3	2.829	2.875	- 1.63
4	2.301	2.440	- 6.04
5	2.806	2.790	0.57
6	3.176	3.112	2.02
7	1.998	1.700	14.91
8	2.457	2.195	10.66
9	2.931	2.741	6.48
10	0.821	0.930	-13.28
11	1.200	1.465	-22.08
12	1.898	2.202	-16.02
13	1.718	1.964	-14.32
14	1.628	1.775	- 9.03
15	1.421	1.620	-14.00
16	1.593	1.450	8.98
17	1.540	1.425	7.47
18	1.400	1.475	- 5.36
19	0.661	0.742	-12.25
20	0.764	0.915	-19.76
21	0.914	1.165	-27.46
22	1.614	1.455	9.85
23	1.645	1.617	1.70
24	1.668	1.820	- 9.11
25	0.741	0.825	-11.34
26	0.962	1.100	-14.35
27	1.276	1.480	-15.99
28	0.744	0.700	5.91
29	0.953	0.863	9.44
30	1.227	1.203	1.96
31	2.406	1.952	18.87
32	1.894	1.686	10.98
33	1.991	1.634	17.93
34	1.561	1.570	- 0.58

TABLE VI (Continued)

Ident. Number	Fluidity (cp^{-1}) Exp.	Fluidity (cp^{-1}) Calc.	% Dev.
35	1.230	1.343	- 9.19
36	0.974	1.087	-11.60
37	1.670	1.546	7.43
38	1.449	1.295	10.63
39	1.073	1.066	0.65
40	1.068	1.109	- 3.84
41	1.165	1.059	9.10
42	0.871	0.869	0.23
43	1.676	1.704	- 1.67
44	1.630	1.487	8.77
45	1.355	1.320	2.58
46	1.439	1.295	10.01
47	1.108	1.126	- 1.62

abs. ave. dev. = 9.79%
ave. dev. = -2.11%

Note: % Dev. = $\left(\frac{\text{Exp.} - \text{Calc.}}{\text{Exp.}}\right)$ (100)

TABLE VII

VALUES OF FLUIDITY CALCULATED WITH PROPOSED CORRELATION (EQUATION (27)) COMPARED TO EXPERIMENTAL VALUES AT 45°C

Ident. Number	Fluidity (cp^{-1}) Exp.	Fluidity (cp^{-1}) Calc.	% Dev.
I	4.077	4.009	1.67
II	1.542	1.975	-28.08
III	2.159	2.530	-17.18
IV	1.961	1.595	18.66
V	0.835	0.778	6.83
1	2.183	2.425	-11.09
2	2.823	2.961	- 4.89
3	3.465	3.476	- 0.32
4	2.863	2.984	- 4.23
5	3.411	3.363	1.41
6	3.817	3.718	2.59
7	2.455	2.052	16.42
8	2.976	2.615	12.13
9	3.530	3.251	7.90
10	1.111	1.238	-11.43
11	1.556	1.800	-15.68
12	2.373	2.660	-12.09
13	2.219	2.420	- 9.06
14	2.101	2.278	- 8.42
15	1.872	2.100	-12.18
16	2.004	1.675	16.42
17	1.957	1.759	10.12
18	1.820	1.891	- 3.90
19	0.920	0.972	- 5.65
20	1.050	1.200	-14.29
21	1.242	1.525	-22.79
22	2.029	1.775	12.52
23	2.080	2.007	3.51
24	2.120	2.258	- 6.51
25	1.009	1.066	- 5.65
26	1.265	1.400	-10.67
27	1.645	1.892	-15.02
28	1.011	0.922	8.80
29	1.249	1.125	9.93
30	1.566	1.312	16.22
31	2.946	2.528	14.19
32	2.394	2.190	8.52
33	2.462	2.080	15.52
34	1.979	2.098	- 6.01

TABLE VII (Continued)

Ident. Number	Fluidity (cp^{-1})		% Dev.
	Exp.	Calc.	
35	1.606	1.780	-10.83
36	1.297	1.450	-11.80
37	2.089	2.000	4.26
38	1.822	1.670	8.34
39	1.399	1.418	- 1.36
40	1.405	1.463	- 4.13
41	1.507	1.378	8.56
42	1.161	1.149	1.03
43	2.137	2.127	0.47
44	2.041	1.990	2.50
45	1.736	1.763	- 1.56
46	1.819	1.727	5.06
47	1.441	1.508	- 4.65

abs. ave. dev. = 9.10%

ave. dev. = -0.82%

TABLE VIII

VALUES OF FLUIDITY CALCULATED WITH PROPOSED CORRELATION (EQUATION (27)) COMPARED TO VALUES FROM THE LITERATURE (11, 14, 15, 43) AT 25°C

Mixture	Mole % First Named Component	Fluidity (cp^{-1})		% Dev.
		Lit.	Calc.	
Benzene plus Toluene	0.00	1.808	1.669	7.69
	11.59	1.775	1.706	3.89
	22.77	1.751	1.744	0.40
	33.58	1.747	1.787	- 2.29
	44.02	1.757	1.826	- 3.93
	54.12	1.767	1.860	- 5.26
	63.89	1.779	1.896	- 6.58
	73.35	1.792	1.928	- 7.59
	82.51	1.792	1.967	- 9.77
	91.39	1.763	2.001	-13.50
	100.00	1.650	2.029	-22.97
Benzene plus Naphthalene	71.11	1.063	0.863	18.81
	75.29	1.125	0.998	11.29
	79.29	1.193	1.126	5.62
	83.11	1.263	1.269	- 0.48
	86.78	1.337	1.416	- 5.91
	90.29	1.413	1.565	-10.76
	93.66	1.490	1.728	-15.97
	96.89	1.570	1.887	-20.19
	100.00	1.653	2.059	-24.56
Benzene plus Diphenyl	74.76	0.952	0.762	19.96
	78.57	1.032	0.897	13.08
	82.16	1.113	1.039	6.65
	85.55	1.198	1.189	0.75
	88.76	1.286	1.347	- 4.74
	91.79	1.376	1.513	- 9.96
	94.67	1.469	1.677	-14.16
	97.40	1.560	1.855	-18.91
	100.00	1.655	2.047	-23.69
n-Hexadecane plus n-Hexane	64.41	0.595	0.444	25.38
	52.51	0.760	0.734	3.42
	42.01	0.960	1.034	- 7.71
	15.64	1.946	2.133	- 9.61
	5.53	2.740	2.802	- 2.26

TABLE VIII (Continued)

Mixture	Mole % First Named Component	Fluidity (cp^{-1}) Lit.	Calc.	% Dev.
n-Hexadecane plus Benzene	57.15	0.564	0.395	29.96
	45.63	0.677	0.616	9.01
	31.05	0.870	0.956	- 9.89
	27.27	0.934	1.052	-12.63
	14.36	1.213	1.463	-20.61
n-Tetradecane plus n-Hexane	53.91	0.977	1.068	- 9.31
	29.25	1.592	1.784	-12.06
	16.47	2.151	2.300	- 6.93
	10.84	2.487	2.585	- 3.94
	5.45	2.886	2.899	- 0.45

abs. ave. dev. = 10.74%
ave. dev. = - 3.65%

Mixture	Mole % First Named Component	Fluidity (cp^{-1}) Lit.	Calc.	% Dev.
Benzene plus Methyl Ethyl Ketone	0.00	2.494	4.643	-86.17
	9.80	2.433	4.343	-78.50
	19.80	2.353	4.047	-71.99
	29.80	2.257	3.796	-68.19
	39.80	2.198	3.515	-59.92
	49.80	2.110	3.241	-53.60
	59.90	2.012	2.989	-48.56
	69.90	1.927	2.759	-43.18
	79.90	1.832	2.520	-37.55
	89.90	1.712	2.283	-33.35
	100.00	1.616	2.054	-27.10

TABLE IX

VALUES OF ULTRASONIC VELOCITY CALCULATED WITH RAO'S CORRELATION COMPARED TO EXPERIMENTAL VALUES AT 25°C

Ident. Number	Ultrasonic Velocity (m/sec.)		% Dev.
	Exp.	Calc.	
13	1285	1288.57	-0.28
14	1301	1288.81	0.94
15	1309	1300.29	0.67
16	1284	1292.72	-0.68
17	1276	1292.58	-1.30
18	1283	1300.60	-1.37
19	1278	1308.97	-2.42
20	1285	1305.13	-1.57
21	1292	1304.76	-0.99
22	1292	1292.81	-0.06
23	1297	1292.63	0.34
24	1303	1294.47	0.65
25	1285	1301.85	-1.31
26	1298	1288.35	0.74
27	1304	1279.46	1.88
28	1293	1306.10	-1.01
29	1295	1298.54	-0.27
30	1294	1292.07	0.15
31	1295	1275.53	1.50
32	1315	1287.33	2.10
33	1304	1285.39	1.43
34	1323	1290.82	2.43
35	1324	1297.40	2.01
36	1316	1302.92	0.99
37	1318	1287.77	2.29
38	1302	1291.05	0.84
39	1305	1299.92	0.39
40	1300	1296.10	0.30
41	1300	1293.22	0.52
42	1301	1300.51	0.04
43	1296	1286.88	0.70
44	1326	1287.53	2.90
45	1320	1292.95	2.05
46	1318	1290.77	2.07
47	1305	1297.68	0.56

abs. ave. dev. = 1.14%

ave. dev. = 0.14%

TABLE X

VALUES OF ULTRASONIC VELOCITY CALCULATED WITH RAO'S CORRELATION COMPARED TO EXPERIMENTAL VALUES AT 45°C

Ident. Number	Ultrasonic Velocity (m/sec.)		
	Exp.	Calc.	% Dev.
13	1199	1182.19	1.40
14	1193	1169.91	1.94
15	1190	1170.62	1.62
16	1210	1199.06	0.90
17	1202	1185.64	1.36
18	1184	1179.91	0.35
19	1208	1207.09	0.08
20	1201	1196.96	0.34
21	1189	1186.30	0.23
22	1220	1208.44	0.95
23	1214	1205.08	0.73
24	1214	1203.36	0.88
25	1211	1205.29	0.47
26	1205	1193.07	0.99
27	1196	1183.57	1.04
28	1216	1210.03	0.49
29	1208	1205.33	0.22
30	1213	1203.08	0.82
31	1166	1158.20	0.67
32	1182	1167.49	1.23
33	1190	1178.96	0.93
34	1180	1173.86	0.52
35	1192	1180.26	0.98
36	1185	1196.24	-0.95
37	1187	1181.88	0.43
38	1190	1194.03	-0.34
39	1193	1199.69	-0.56
40	1198	1188.59	0.79
41	1209	1195.25	1.14
42	1211	1200.06	0.90
43	1207	1186.10	1.73
44	1187	1176.32	0.90
45	1194	1182.22	0.99
46	1185	1188.46	-0.29
47	1187	1193.63	-0.56

abs. ave. dev. = 0.82%
ave. dev. = 0.67%

APPENDIX B

MISCELLANEOUS

TABLE XI

VALUES FOR K(T) AT VARIOUS TEMPERATURES (17)

T(°C)	K(T)
0	588
10	604
20	618
25	625
30	631
40	642
50	652

TABLE XII

VALUES FOR THE CONSTANTS IN RAO'S EQUATION (32)

Series	α	β
Paraffins	13.97	155
Esters of Acetic Acid	14.01	-206
Monohydric Alcohols	14.00	- 32
Benzene Hydrocarbons	14.02	-120
Ketones	13.99	- 48

TABLE XIII

VALUES FOR RAO'S CONSTANT FOR THE COMPOUNDS CONSIDERED IN THIS WORK

Compound	R'
n-Hexane	1356
n-Tridecane	2731
n-Tetradecane	2926
n-Hexadecane	3318
Cyclohexane	1196
Benzene	979
Toluene	1170
Ethylbenzene	1368
Naphthalene	1677
Diphenyl	2042
Methyl Ethyl Ketone	961

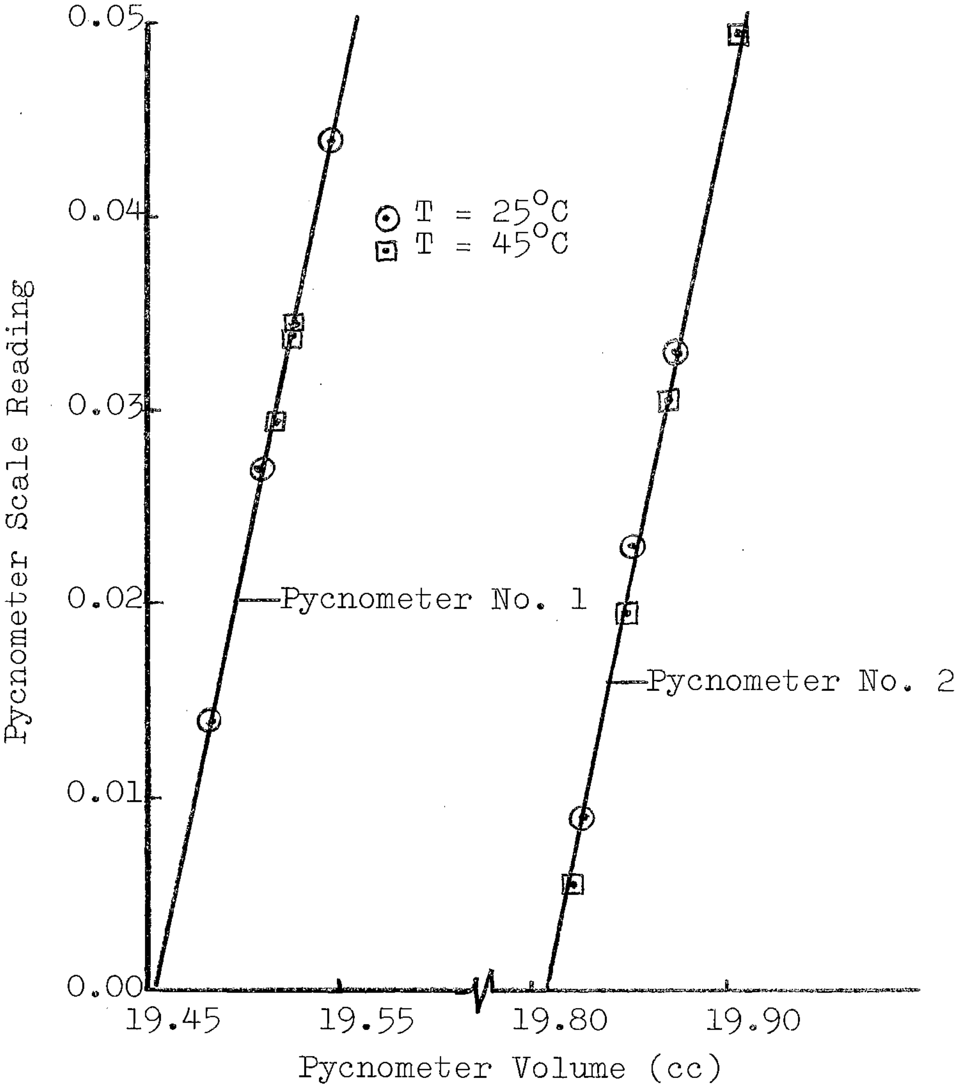

Figure 39. Pycnometer Scale Reading as a Function of Pycnometer Volume

Nomenclature

Quantity	Symbol	Units
Acentric Factor	ω (Omega)	--
Area, molecule surface of one mole of liquid	Y	cm^2
Atomic Weight	A_W	gm/gm atom
Compressibility, adiabatic	β_{ad} (Beta)	cm^2/dyne
Constant,		
In equations (2) and (3)	c	--
In equation (6)	d	--
In equations (8) and (9)	a'	--
In equation (10)	a	--
In equation (10)	b	--
In equation (17)	p	--
In equation (17)	k'	--
In equation (23)	α (Alpha)	--
In equation (23)	β (Beta)	--
In equations (25) and (27)	c_1	--
In equations (25) and (27)	k_1	--
Boltzmann's	k	erg/$^{\circ}$C
Planck's	h	erg sec.
Rao's	R'	--
Universal gas	R	cal/gm mole $^{\circ}$K
Viscometer	C	cs/sec.
Wada's	W	--
Density	ρ (Rho)	gm/cm^3
Energy,		
Activation, for flow	$E_{vis.}$	cal/gm mole
Of vaporization	$\Delta E_{vap.}$	cal/gm mole
Of vaporization, for component i	ΔE_i	cal/gm mole

Quantity	Symbol	Units
Fluidity	ϕ(Phi)	cp^{-1}
Free energy,		
Of activation	ΔG	cal/gm mole
Of activation, component i	ΔG_i	cal/gm mole
Of activation, interaction of components i and j	ΔG_{ij}	cal/gm mole
Excess, of mixing	ΔF_m	cal/gm mole
Function of temperature,		
In equations (2), (3), and (13)	A	--
In equation (7)	B	--
In equations (20) and (25)	K(T)	--
In equation (26)	a_1, a_2, a_3	--
In equations (26) and (27)	K'	--
Length, intermolecular free	L	Å
Molecular weight,	M	gm/gm mole
Of component i	M_i	gm/gm mole
Mole Fraction, component i	x_i	--
Number,		
Avogadro's	N	molecules/gm mole
Packing	c'	--
Property, intermolecular	j	--
Ratio of specific heats	γ(Gamma)	--
Temperature,	T	°C
Melting	T_m	°C
Time	t	sec.
Velocity, ultrasonic	u	m/sec.
Viscosity,		
Absolute	μ (Mu)	cp.
Absolute, contribution by solid-like molecules	μ_s (Mu)	cp.

Quantity	Symbol	Units
Absolute, contribution by gas-like molecules	μ_g(Mu)	cp.
Kinematic	ν(Nu)	cs.
Kinematic, of component i	ν_i(Nu)	cs.
Kinematic, interaction of components i and j	ν_{ij}(Nu)	cs.
Volume,		
Available	V_a	cm^3
Free	v_f	cm^3
Molar, at temp. T	V_T	cm^3/gm mole
Molar, at temp. at which $\phi = 0$	V_o	cm^3/gm mole
Molar, of a mixture	$V_{mix.}$	cm^3/gm mole
Molar, of unexpanded solid	V_S	cm^3/gm mole
Of a gram atom @ T_m	V_A	cm^3
Specific	v	cm^3/(gm/gm mole)

Location of Original Data

The original data taken in the experimental work of this thesis are in the possession of Professor John H. Erbar of the School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma.

The design and experimental work of this thesis were performed in Lab 307, Engineering North, Oklahoma State University, Stillwater, Oklahoma, between September, 1964 and May, 1966.

VITA

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