A STUDY OF THE RELATIONSHIP BETWEEN ULTRASONIC VELOCITY AND THE VISCOSITY OF ASSOCIATING LIQUID MIXTURES

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PREFACE

The purpose of this work is to establish the relationship between the ultrasonic velocity in an associating liquid and its viscosity. A correlation (based upon literature data) for the viscosity in terms of a simple function of the ultrasonic velocity is presented and analyzed. The nature of the liquid state and the phenomena of momentum transport and ultrasonic transmission in liquids are discussed in some detail in terms of the fundamentals of thermodynamics and intermolecular interactions. That there is a definite relationship between the ultrasonic velocity and the viscosity in associating (and non-associating) liquids has been established, and more work along the lines presented here is recommended.

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CHAPTER I

INTRODUCTION

Motivation for This Work

It is not necessary to emphasize the importance to the chemical process industries of methods for determining accurately and cheaply the physical properties of liquids and liquid mixtures. Let it suffice here to refer the reader to a recent article by Reid (32) in which this question is examined in some detail. He summarizes the state of the art concerning the viscosity (and its state dependence) of liquids and liquid mixtures. The present estimation techniques for the viscosity of liquids and liquid mixtures are rated as "Poor-Better Ones Needed." He classes the adequacy of the available data as "Usually Sufficient" for pure liquids and "More Definitely Needed" for liquid mixtures. These needs are the primary incentives for this work.

The purpose of the following study is the examination of the nature of mixtures of associating and non-associating liquids with respect to their viscosity, density, and ability to transmit ultrasonic energy. Water, methyl alcohol, and ethyl alcohol represent the range of associating liquids used in the binary mixtures to be studied here; and benzene, toluene, and ethyl benzene are the non-associated liquids. Water is a "lattice" associated liquid with degrees of association as high as several hundred, whereas methyl alcohol and ethyl alcohol are "cluster" associated liquids with much lower association numbers (typically 2 or 3). Mixtures of these liquids therefore present the spectrum of association numbers in liquids. The non-associating liquids in mixture with some of these associating liquids illustrate the well-known ability of aromatic species to break hydrogen bonds (10). Five binary systems (water-methyl alcohol, water-ethyl alcohol, toluene-methyl alcohol, benzene-ethyl alcohol, and ethyl benzene-ethyl alcohol) will be studied in more or less detail respecting the effects of molecular configurations in solution upon their viscosity and ultrasonic velocity. Both maxima and minima occur in the viscosity versus composition curves of these mixtures. A correlation for the viscosity of associating liquids in terms of a simple function of the ultrasonic velocity will also be presented and analyzed. The hope is this investigation will lead not only to a better understanding of the liquid state, but also to the extended use of ultrasonic energy sources as analytical tools.

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

The following section will be devoted to brief sketches of a general nature concerning (1) theories of the liquid state, (2) the theory and methods of the ultrasonic investigation of matter, and (3) theories respecting the viscosity of liquids and liquid mixtures.

Theories of the Liquid State

The theories of the liquid state and the explanations of the various phenomena observed in liquids vary widely in nature and complexity. It seems that many liquid models are developed for specialized service in visualizing the particular theory or mechanism under discussion. For example, consider the rather detailed liquid model developed by Gross and Zimmerman (8) for describing the temperature dependence of viscosity. They visualize a generalized liquid as composed of clusters of "inactive" molecules separated by mono-molecular zones of "active" molecules. This model can be crudely described as rigid structures of low energy molecules suspended in a matrix of high energy molecules. Flow is considered as taking place in laminae of thickness equal to that of the "inactive" clusters; the "active" molecules thus act as a kind of microscopic lubricant through which the "inactive" clusters flow. Their correlation (thus far tested successfully on the first twenty pure paraffin hydrocarbons) has the form

$$\mu V^{1/3} = \mu N^{1/3} + \zeta g$$

where q and ζ are empirical, temperature dependent constants, and d is the average diameter of the individual molecules. The physical significance of q and ζ (along with other parameters introduced during the derivation) is belabored in some detail by Gross and Zimmerman, but as yet the theory is too complex to be of general usefulness.

In general, however, the approaches used by most investigators fall into one or more of three areas. They are (1) treatment of liquids as highly compressed gases, (2) ascribing to liquids a pseudo-crystalline (solid) structure with short-range order and long-range disorder, and (3) analysis of liquid behavior directly from the fundamentals of intermolecular interactions and statistical mechanics. The first of these has found some success in analyzing the physico-chemical properties of liquids near their critical temperatures.

For instance, Nozdrev (26) discusses the work of Kittel on the ultrasonic velocity in a liquid following the equation

$$pV = 3NkT$$

By using the rigorous equation

$$u^2 = \left(\frac{\partial p}{\partial \rho}\right)_S$$

(see any good thermodynamics text) he has shown that

$$u_{liq} = \frac{V}{V_{fr}}\left(\frac{C_v + 3R}{C_v}\right)^{1/2}\left(\frac{3kT}{M}\right)^{1/2}$$

This expression is similar to that developed by Eyring (to be discussed later) which is based on a <u>liquid model</u> rather than an <u>equation of state</u>. However, the high densities and consequent strong intermolecular interactions in liquids render even the most approximate quantitative arguments applicable only to very special cases.

Theories taking advantage of the similarities between the solid (crystalline) state and the liquid state have been much more effective in discussions of liquid physical properties than the compressed gas arguments. That this should be so could be predicted from the fact that there is a relatively small volume expansion for most substances during the fusion of a crystalline sample (about 10%) as compared with the volume of expansion on vaporization or sublimation. This implies that liquid density and intermolecular spacing are much nearer those of a solid than a gas. Frenkel (5) seems to have been the first to develop the vacancy theory of liquids in connection with their transport properties. A liquid is assumed to be composed of molecules more or less closely packed along with molecular size spaces randomly interspersed. The liquid flows (at the molecular level) by "holes" and molecules exchanging places, and the detailed theory is based on established crystal structure. Frenkel concludes his section on the viscosity of ordinary liquids by summarizing this connection between solid and liquid structures.

> In a first approximation they are wholly deprived of fluidity, which can be obtained in the second approximation by taking into account the elementary displacements of the equilibrium positions of each particle in the crowd formed by the surrounding particles.

On the basis of this conception the following expression in terms of molecular dimensions and structure (A) and the potential energy W (activation energy) is developed.

$$\mu = A e^{W/kT}$$

The diffusion coefficient is a similar function of molecular and structural parameters and the activation energy for flow (W). Frenkel and others have developed and exploited this approach to a considerable degree, but its general usefulness appears limited to temperatures near the melting point. See also Eyring (24) on this point.

Eyring and his collaborators (2, 4, 7, 24) during the past thirty years have developed a cogent theory of the liquid state based on a unique combination of approaches (2) and (3). In the "hole theory" Eyring visualizes a liquid as composed of molecules (generally spherical) and "holes" of approximately molecular size. (The basic picture is quite similar to the earlier approach of Frenkel.) To this model he applies the general principles of statistical mechanics.

Recent developments of this tack involve the concept of three "significant structures" in a liquid---(1) "gas-like" molecules; (2) "solid-like" molecules; and (3) molecules exhibiting an intermediate positional degeneracy, because they are each surrounded by both other molecules and "holes". Eyring clarifies this model (4).

It should be stressed that our theory does not regard the liquid state as a mixture of solid and gas. A molecule has solid-like properties for the short time it vibrates about an equilibrium position, then it instantly transforms to gas-like behavior as it jumps into the neighboring vacancy. It is well known that nucleation of bubbles in boiling and crystal nucleation in freezing, if uncatalyzed, are very slow processes. These facts show that no solid or gasious molecular arrangement as large as these nuclei exists in the liquid state.

He uses this model and the principles of statistical mechanics to develop general expressions for the transport and physical properties of liquids. For example, the expression for liquid viscosity takes the form (4)

$$\mu = \frac{V_s}{V}\mu_s + \frac{V-V_s}{V}\mu_g$$

where μ_s is the contribution of the solid-like molecules, V_s/V is the fraction of solid-like species, μ_g is the contribution of the gas-like molecules and $(V-V_s)/V$ is the fraction of gas-like species. The relationships for μ_s and μ_g are very complex, and successful application has been made only on simple liquids such as argon. Compare the more readily applicable model of Gross and Zimmerman (8) with the "significant structures" of Eyring.

Hildebrand (10, 11) maintains that simple liquids in general possess no long-range order; there is only a very short-range order which comes from the requirement that the molecular or atomic species do not overlap. On the basis of x-ray scattering experiments Hildebrand concludes that the implicit or explicit assumption of quasi-lattice order in liquids is not justified. Note, however, that other workers hold the opposite viewpoint---also based on x-ray data (25).

Hildebrand's theory of regular solutions assumes the excess entropy of mixing to be zero (i. e., maximum randomness), and that all non-idealities of mixing are tied up in the excess enthalpy caused by differences in the internal pressures of the pure liquids. This is valid for most non-associated liquids of approximately spherical symmetry. He disdains the use of such terms as "lattice sites", "free volume", "cell theories", "hole theory", and "gas-like and solid-like molecules" which are widely used in discussing liquid structure. Concerning this point Hildebrand (11) concludes

> ...the most detailed free volume theories cannot be made consistent with all the thermodynamic properties of a liquid, although some workers continue to try. Free volume is <u>not</u> a physical parameter and cannot be a thermodynamic one. All detailed free volume models of liquids involve basically unrealistic assumptions concerning liquid structure.

More will be said later concerning this point of view.

It is appropriate at this point to treat briefly the types of intermolecular interactions which are of importance in the study of non-electrolytic liquids (10, 11, 25, 36). The nature and existence of intermolecular forces is well illustrated by Table I (25). The external pressure, p, is applied to the liquid, and p_i is the internal pressure (intermolecular force) which is defined by the thermodynamic equation of state (25)

$$\left(\frac{\partial U}{\partial V}\right)_T = P_i = T\left(\frac{\partial p}{\partial T}\right)_V - P$$

As the external pressure, p, is increased, the internal pressure, p_i, decreases from high positive (attractive) values to high negative (repulsive) values. Thus, the well-known fact that repulsive forces exist at small intermolecular distances is readily demonstrable by means of this simple experiment.

TABLE I

DIETHYL ETHER @ 25°C

p (atm.):	200	800	2000	5300	7260	9200	11,100
p_i (atm.):	2790	2840	2530	2020	40	-1590	-4380

The three main types of intermolecular interactions (after van der Waals) existing in non-electrolytes are (1) the orientation effect between permanent dipoles, (2) the induction effect between a permanent dipole and a polarizable molecule, and (3) the London dispersion forces between two molecules or atoms with no dipole moments. The intermolecular potential energy resulting from each of these effects varies as the minus sixth power of the intermolecular distance; i. e., $U_0 \propto r^{-6}$. Differentiating U_0 with respect to r results in the intermolecular force (internal pressure)--- $F = -\frac{\partial U_0}{\partial r}$.

Keesom in 1912 developed an expression for the interaction of two permanent dipoles,

$$U_0 = -\frac{2}{3}\frac{\bar{\mu}^4}{r^6}\cdot\frac{1}{kT}$$

based on the statistical variation in their relative orientations. (These expressions for U_0 are for pure liquids; similar equations are developed for mixtures in terms of pure component parameters.) Debye a few years later modified this result to account for the induction of dipole moments into normally non-polar (or weakly polar) molecular species---

$$U_0 = -\frac{2\alpha\bar{\mu}^2}{r^6}$$

These expressions are fine when there are polar molecules present in the liquid; but in simple liquids a new concept was required to explain their ability to condense. London in 1930 developed such a concept, resulting in the following expression.

$$U_0 = -\frac{3}{4}h\nu_0\frac{\alpha^2}{r^6}$$

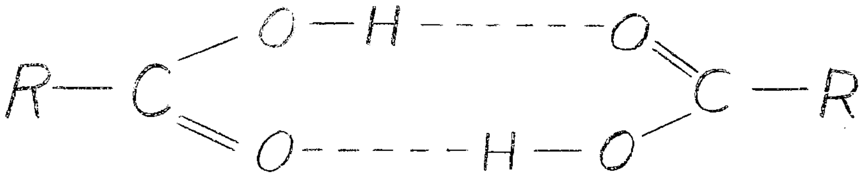
His own description of the theory is perhaps the most lucid (10).

> Though it is of course not possible to describe this interaction in terms of our customary classical mechanics, we may still illustrate it in a kind of semi-classical language.
>
> If one were to take an instantaneous photograph of a molecule at any time, one would find various configurations of nuclei and electrons, showing in general dipole moments. In a spherically symmetrical rare gas molecule, as well as in our isotropic oscillators, the average over very many of such snapshots would of course give no preference for any

direction. These very quickly varying dipoles, represented by the zero-point motion of a molecule, produce an electric field and act upon the polarisability of the other molecule and produce there induced dipoles, which are in phase and in interaction with the instantaneous dipoles producing them.

These three efects are present to varying degrees in all liquids and liquid mixtures. The proportion of their individual influences determines the liquid's properties. The important factor to remember about these interactions is that they are all of short-range influence (existing over at most a few molecular diameters).

Hydrogen bonding plays the key role in the study of mixtures of associating liquids. Detailed analyses of this phenomenon are also readily available (10, 28), but the basic results and their causes are easily presented in a qualitative fashion. It is well-known that certain low molecular weight liquids possess abnormally high boiling points (e. g., water, ammonia, and hydrogen fluoride), whereas certain compounds of much higher molecular weights boil at significantly lower temperatures (e. g., sulfur dioxide). The reason for this effect is the extensive hydrogen bonding which is caused by the bare proton of a hydrogen atom in compound with a strongly negative atom coming into close proximity (due to its small size) with a second negative atom. Large, rather stable clusters are built up in the liquid, resulting in a much higher effective molecular weight. The formation of dimers by aliphatic acids is a simple example of how molecular structure aids this phenomenon.



Hildebrand (10) summarizes the nature of hydrogen bonding.

> ...the bonding hydrogen does not participate in two covalent bonds but the interaction is essentially electrostatic, the exceptional nature of the bond being due to the closeness of approach of the two dipoles made possible by the small size of the proton...

More will be said on this point later when the data are discussed in terms of molecular arguments.

Ultrasonic Energy Transmission

The basic theory and applications of ultrasonic energy transmission in liquids is treated in a number of excellent works (2, 9, 26, 34). One of the earlier theories for calculating the ultrasonic wave velocity in liquids was presented by Eyring (7). The total velocity is imagined to be made up of a gas-kinetic component (through the intermolecular free length) and an essentially infinite component (across each molecular species). Thus, the free length between the molecules is the limiting factor in the determination of the speed of a sonic front in liquids. Eyring's equation, based on this model and thermodynamics, has the form

$$u_{liq} = \left(\frac{V}{V_f}\right)^{1/3}\left(\frac{RT\gamma}{M}\right)^{1/2} = \left(\frac{V}{V_f}\right)^{1/3} u_{gas}$$

Note the similarity between this equation and that developed by Kittel on the basis of an equation of state and thermodynamic relations. The main problem is the difficulty in determining the free volume V_{fr}---i. e., the intermolecular free length cubed. This problem is discussed in some detail in a later section. Although this approach found some success, it has been criticized on the ground that it neglects intermolecular forces. It is the opinion of this writer that Eyring's picture is substantially correct. Because of the extreme speed of a sonic front through a liquid (approximately 1200-1500 meters per second), the intermolecular forces are relatively ineffective in directly influencing its transmission. Indirectly, however, the intermolecular forces are responsible for the ultrasonic velocity because of their role in determining the distances between liquid molecules.

A rigorous derivation of the basic equation

$$u^2 = \frac{1}{\beta_{ad}\rho} \tag{1}$$

is given by Blitz (2), and is reproduced in Appendix B. This equation will be used later in developing useful expressions of value in correlating the viscosity with simple functions of the ultrasonic velocity.

Nozdrev (26), Bergmann (1), Herzfeld and Litovitz (9), and Richardson (34) present fine general and specific discussions relating to the dependence of the ultrasonic propagation constants (velocity and absorption) on a number of factors. These include (1) temperature and pressure effects, (2) range of the propagation constants in various types of liquids (e. g., polar), and (3) dependence of the propagation constants on the ultrasonic frequency. Nozdrev's (26) comments are particularly illuminating in this regard, because he experimentally separates these factors and evaluates them independently of one another. For instance, the quantity du/dT (i. e., the total derivative) is frequently found in the literature, whereas a much more useful and meaningful term is $\left(\frac{\partial u}{\partial T}\right)_{P,\rho}$. These values may differ not only in magnitude but also in sign. Separation of the effects of changes in state variables upon physical properties is rare in the literature (because of the experimental problems involved), but their value in developing an understanding of the nature of the physical phenomenon is great. Specific examples of the effects of state of aggregation and temperature upon the ultrasonic velocity are presented in a later section; let it suffice to say here that *a priori* generalizations in the case of associated liquids are as yet impossible (22).

Of the various devices used to study ultrasonic propagation constants, the following general catagories may be mentioned. For research purposes there are (1) the use of optical devices which relate the effect on light waves of a sample (gas or liquid) which is transmitting ultrasonic waves to the propagation constants, and (2) pulse-type equipment by which the propagation constants are measured directly by electronic means. The third class of devices are those built for special applications---e. g., medical diagnosis and structural flaw detection.

The most popular of the optical techniques is the optical diffraction method. As a succession of sonic fronts travels through the liquid, a diffraction grating is set up (caused by the resultant density fluctuations). A monochromatic light source is then trained perpendicular to the direction of sonic propagation, and the wavelength of the ultrasonic waves is found from the Bragg relation

$$\lambda = \frac{2n\Lambda}{\sin\theta}$$

where n is an integer, Λ is the wavelength of the light source and θ is the angle of diffraction.

Since the advent of radar, the sophistication of electronic circuitry has reached the level required for the direct measurement of ultrasonic velocities. In the pulse technique a series of pulses is sent through a measured length of liquid and timed electronically. This approach is being used more often in research and industry, because the results are obtained more quickly.

There are a multitude of transducers which are used for generating ultrasonic waves in gases and liquids, but most work on the principle of piezoelectricity. Certain crystalline solids when subjected to an electric potential are mechanically strained; and when the potential is released, the strain is relaxed. Subjecting piezoelectric crystals to alternating currents causes them to oscillate and send plane sonic waves through the medium in contact with them.

Viscosity of Liquids and Liquid Mixtures

The investigation of the nature of the viscosity of liquids and liquid mixtures has been developed on a number of fronts, ranging from complete empiricism to theoretical analyses based on detailed liquid models and the fundamentals of statistical mechanics. In spite of these efforts nothing of wide general applicability has as yet been developed. Friend (6) in 1938 wrote of a simple, qualitative picture of momentum transport in liquids---it is this very general model which is the descriptive basis of the analyses of this work.

> We may regard liquid viscosity as the resultant effect due to an impeding of the flow of parallel layers of liquid caused by the attraction exerted by each molecule in the one layer upon the adjacent molecule in the other.

The most popular model for the semi-empirical analysis of liquids and liquid mixtures is that developed by Eyring and coworkers based on the theory of absolute reaction rates (7). While many workers (8, 23) have used the model suggested by this approach for special purposes and to justify other semi-empirical correlations, Eyring and his coworkers have applied statistical mechanics to erect a general (temperature dependent) theory of the flow of liquids---including both non-newtonian and newtonian behavior (3). The equation which was developed on this basis is

$$\tau = \sum_{i=1}^{\bar{n}} \frac{\bar{X}_i}{B'_i} \sinh^{-1} \frac{\dot{S}}{A_i}$$

where

$$B'_i = \frac{(\lambda_2 \lambda_3 \lambda)_i}{2 k T}$$

$$A_i = 2 \left(\frac{\lambda_1}{\lambda}\right)_i \frac{kT}{h} \exp - \frac{\Delta H_i^{\ddagger}}{RT} + \frac{\Delta S_i^{\ddagger}}{R}$$

$\bar{n}$ = the number of significantly different flow units

For newtonian flow this equation reduces to

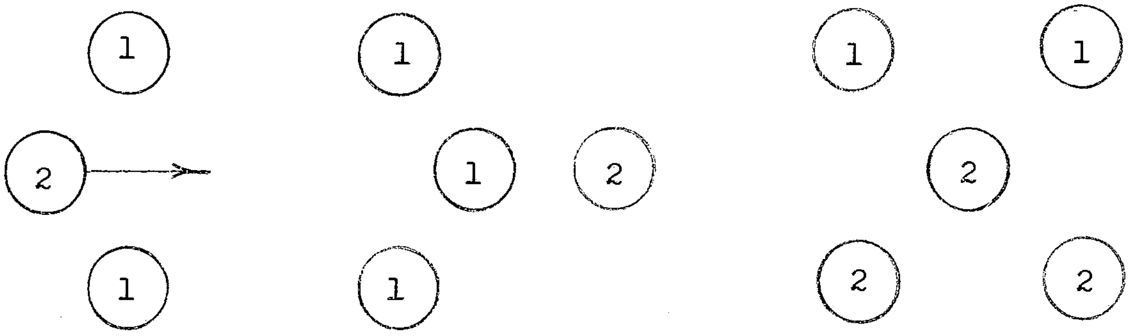
$$\tau = \frac{1}{B'} \left(\frac{\dot{S}}{A}\right) = \mu \dot{S}$$

and

$$\mu = \frac{1}{A B'}$$

The assumptions involved in this reduction include (1) there is only one significant flow unit and (2) $\sinh^{-1} (\dot{S}/A)$ is small and approximately equal to $\dot{S}/A$. Eyring (7) developed the newtonian form of this equation many years ago based upon the incipient hole theory and the concept of absolute reaction rates.

Of the semi-empirical correlations for binary mixtures, the recent work by McAllister (23) (based on Eyring's model) appears to be the best for associating species, though the method has now been extended to ternary systems (20). His correlation for the kinematic viscosity of binary mixtures was developed from an analysis of multibody interactions in solution, as shown below.



(a) (b) (c)

In (a) a three-body interaction in a binary mixture is depicted; molecule 2 is moving over the potential barrier between two type-1 molecules. On the basis of this model, McAllister and his students derived the following two-parameter equation.

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

The only empirical terms are ν_{12} and ν_{21}, determined by a least squares analysis. They have also developed an equation for interactions of the type of interactions in (b) and (c). (The central species are considered moving normal to the page.) These equations are very complex and involve 3 and 4 experimental parameters, respectively. Solutions to these equations require a computer and rather extensive viscosity data. It appears that to analyze mixtures involving molecules of greatly different size, 7 or higher body interactions need to be considered. This is hopelessly complex if physical insight and useful correlations are required. The correlation is quite flexible, but is not very useful if absolute viscosities are needed. Finally, no account is taken of such important solution phenomena as association (directly), solvation and steric effects (except relative molecular sizes).

The work of Jacobson (16) on the viscosity of liquids and liquid mixtures, based upon the intermolecular free length in solution, is the foundation of the work presented here. It will be developed in a later section.

CHAPTER III

DATA SOURCES

No ultrasonic velocity data were taken on any of the systems described in this work; but viscosity and density data were determined on the systems methyl alcohol-toluene, ethyl alcohol-benzene, ethyl alcohol-ethyl benzene, and ethyl alcohol-water (Table II). The remainder of the data used in the study were gleaned from the literature (26, 38).

The density and viscosity data (Table II) were taken on Phillips Pure Grade (toluene, benzene, and ethyl benzene) and Baker Analyzed Grade (methyl alcohol and ethyl alcohol) chemicals. A water bath capable of maintaining the temperatures to ± 0.02°C (33) was used in conjunction with a Zeitfuchs Cross-Arm viscometer (19) and a Robertson Graduated Pycnometer (35). The techniques employed are well-described in the given references, so only a brief outline will be given here.

The chemicals were used in their commercial form without further purification, as their densities and viscosities agreed within two figures in the forth decimal place with accepted literature values (38). Sulfuric acid-potassium permanganate cleaning solution was applied twice (after

TABLE II

DATA

	Mole Fractions						Experimental Values			
Mixture	Ethyl Benzene	Benzene	Ethyl Alcohol	Water	Toluene	Methyl Alcohol	Density g/cm^3 25°C	Viscosity Cp 25°C	Density g/cm^3 45°C	Viscosity Cp 45°C
Pure	1.0000	---	---	---	---	---	0.8623	0.6287	0.8447	0.5048
Pure	---	1.0000	---	---	---	---	0.8730	0.6034	0.8515	0.4631
Pure	---	---	1.0000	---	---	---	0.7851	1.0908	0.7677	0.7616
Pure	---	---	---	1.0000	---	---	0.9971	0.9116	0.9903	0.6095
Pure	---	---	---	---	1.0000	---	0.8619	0.5537	0.8433	0.4410
Pure	---	---	---	---	---	1.0000	0.7862	0.5450	0.7674	0.4150
#1	---	0.2500	0.7500	---	---	---	0.8149	0.8425	0.7952	0.6130
#2	---	0.5000	0.5000	---	---	---	0.8379	0.6760	0.8172	0.4981
#3	---	0.7500	0.2500	---	---	---	0.8566	0.5938	0.8355	0.4494
#4	0.2500	---	0.7500	---	---	---	0.8176	0.8453	0.8000	0.6072
#5	0.5000	---	0.5000	---	---	---	0.8375	0.7032	0.8193	0.5288
#6	0.7500	---	0.2500	---	---	---	0.8515	0.6310	0.8336	0.4932
#7	---	---	0.7499	0.2501	---	---	0.8172	1.4748	0.7994	0.9507
#8	---	---	0.4973	0.5027	---	---	0.8584	1.9433	0.8415	1.1566
#9	---	---	0.2500	0.7500	---	---	0.9186	2.3715	0.9030	1.2930
#10	---	---	---	---	0.9046	0.0954	0.8592	0.5392	0.8404	0.4319
#11	---	---	---	---	0.7629	0.2371	0.8543	0.5412	0.8352	0.4242
#12	---	---	---	---	0.6000	0.4000	0.8445	0.5602	0.8252	0.4315
#13	---	---	---	---	0.4000	0.6000	0.8354	0.5741	0.8163	0.4390
#14	---	---	---	---	0.2500	0.7500	0.8226	0.5801	0.8035	0.4386
#15	---	---	---	---	0.1000	0.9000	0.8041	0.5671	0.7852	0.4270

taking measurements on each set of mixtures) to both the pycnometers and viscometers. After each mixture determination (viscosity and density) the two instruments were thoroughly washed with Pure Grade acetone and carefully dried with a water aspirator. The drying air was drawn through a dessicant to assure that no contamination was introduced during the drying operation.

Density

The Robertson Graduated Pycnometers (two for each mixture) were each weighed with a Mettler balance, capable of indicating accurate readings to four decimal places (.0001 gram) with estimation of the fifth place. After introduction of the liquid into the pycnometer, the weight was again measured. Care must be exercised to assure that an amount of liquid is added such that, after introduction of the loaded pycnometer into the water bath, the thermal expansion of the liquid will not cause the reading to fall off of the graduated arms. A certain amount of experience is required before this will be assured for a variety of systems.

The loaded pycnometer is allowed to remain in the water bath for thirty minutes (to assure temperature equilibrium) before the final reading is taken. From the previous calibrations (in this case with water) the graduated scale readings are a direct measure of the volume of liquid in the instrument. With the weight and volume having thus been determined, the density follows straight away. Reproducabilities to ± 0.0001 gm/cm^3 were obtained in this manner.

Viscosity

The Zeitfuchs Cross-Arm Viscometer was charged to a predetermined level with the liquid to be observed. It was allowed to stand in the water bath for two minutes to allow for temperature equilibrium. A suction bulb was then used to suck the liquid into the capillary, through which it flowed by the action of gravity. The time required for the liquid to fill a bulb at the end of the capillary was measured to one-hundredth of a minute. From previous calibration with U. S. Bureau of Standards calibrating oils the constant c_1 in the equation

$$\nu = c_1 t$$

was determined. Using this expression the kinematic viscosities of all liquids run through the instrument are calculated. This procedure was continued until three identical results were obtained in a row.

CHAPTER IV

METHOD OF CORRELATION

The purpose of this work is to study mixtures of associating and non-associating liquids in terms of the three physical properties---viscosity, density, and ultrasonic velocity. To do this properly it is not only necessary to correlate experimental data, but also to analyze the observations in terms of the fundamentals of thermodynamics and intermolecular interactions. This section will be devoted to the first of these goals---the correlation of viscosity with a simple function of the ultrasonic velocity.

Description of the Method

The basic correlating parameter to be used is the average intermolecular free length between the surfaces of the molecular species in the liquid. This quantity is analogous to the mean free path in a gas. Jacobson (12-18) has shown that functions of the intermolecular free length (L) correlate well certain physical properties which depend on intermolecular interactions. Expressions of the form of equation (2) are of general applicability in this regard.

$$j = k_j \cdot L^{p_j} \qquad (2)$$

Equations (3) and (4) give Jacobson's (12) definition of intermolecular free length.

$$L = \frac{2(V_T - V_0)}{Y} = \frac{2V_a}{Y} \qquad (3)$$

$$Y = f(36\pi N V_0^{2})^{1/3} \qquad (4)$$

Eyring's definition is given by

$$L = \left(\frac{2^{1/2}}{N}\right)^{1/3}\left(V_T^{1/3} - V_0^{1/3}\right) \qquad (5)$$

Both of these definitions are based on geometric considerations; i. e., spherical molecules in hexagonal close packing. At 0°K the spheres are imagined as packed tight against one another, and at higher temperatures the kinetic vibrations cause the spheres to separate to an average distance L. The form of packing is still assumed hexagonal.

Thus, the intermolecular free length (L) is ideally the distance between the surfaces of spherical molecules ($f = 1$) at the given temperature (Figure 1). For most low molecular weight liquids the form factor (f) (see Nomenclature section) is approximately equal to one (21). This definition is, however, not exact; a rigorous calculation of L would require a knowledge of molecular shapes ($f \neq 1$) in the liquid and the type of molecular packing (e. g., cubic or hexagonal packing of spherical molecules), along with an analysis of the very difficult problem of electron cloud interactions. See Eyring and others (24) for other types of packing and molecular configurations. These comments will be expanded in Chapter V.

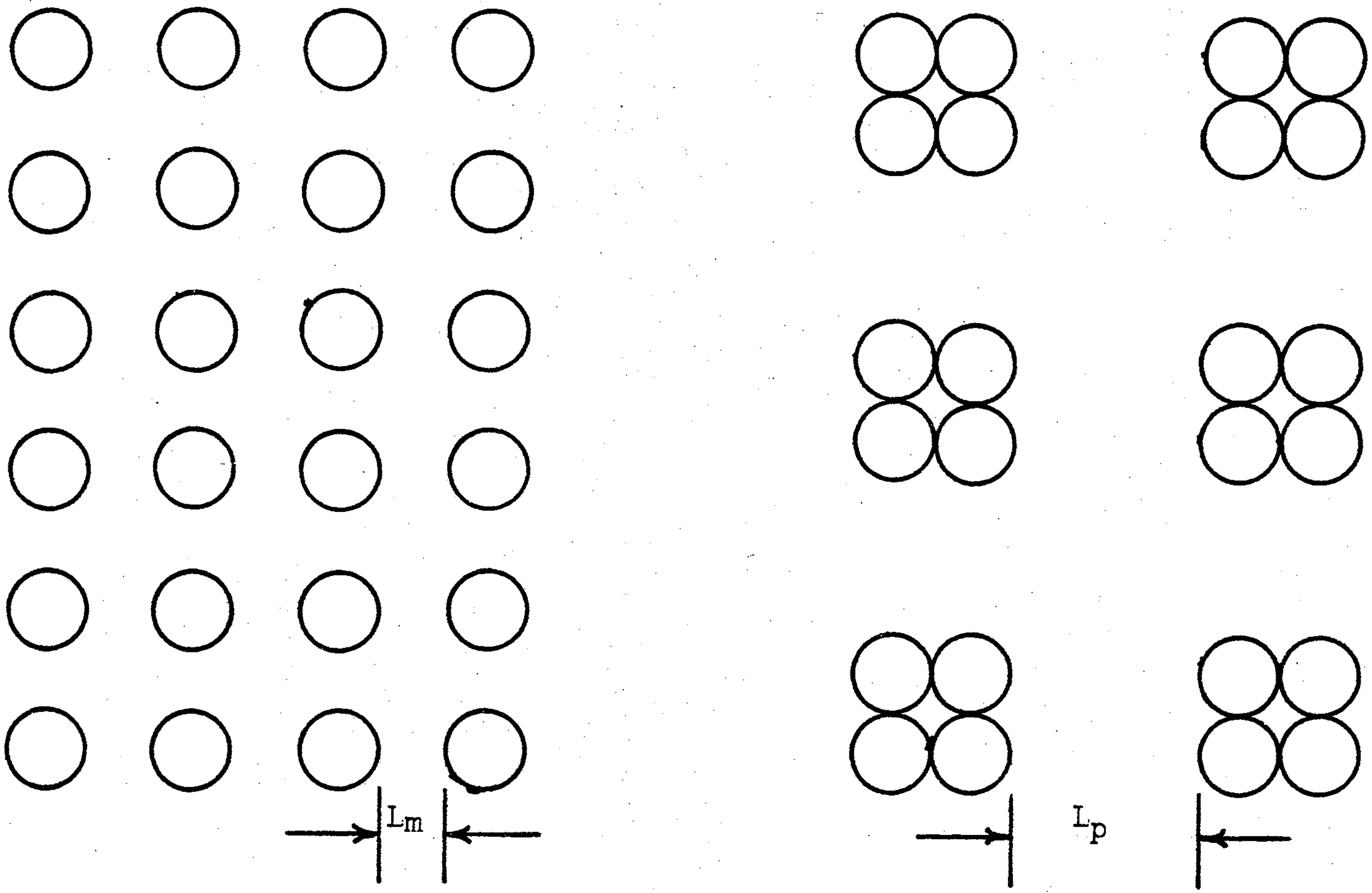


Figure 1. Schematic Showing the Effect on L of X. L_p is the Actual Free Length in the Associated Liquid and L_m is a Hypothetical Free Length Which Would Prevail if the Molecules Were Unassociated and Evenly Distributed.

Viscosity, surface tension, adiabatic and isothermal compressibilities, and diffusion coefficients have been shown (12-18) to be simply related to L for a wide variety of associating and non-associating liquids and liquid mixtures. These relationships all have the form of equation (2); for instance, the following equation has been shown to be valid for a variety of substances

$$\phi = k_j' L_{\phi}^{p_j}$$

To determine the degree of association in a liquid it is only necessary to calculate L from equation (2) and determine V_T from equation (3) or (5). Since , the degree of association can be easily found from M (calculated) and the known value of the molecular weight of the system being studied. Later a simpler method for evaluating the degree of association will be developed and applied to a number of systems.

From the rigorous expression for the adiabatic compressibility

$$\beta_{ad} = \frac{1}{u^2 \rho} \qquad (1)$$

and equation (2) (with j = β_{ad}), equation (6) is readily obtained.

$$u L \rho^{1/2} = K(T) \qquad (6)$$

K(T) is a constant weakly dependent on T (13) (see Appendix A for complete derivation). Note that p in equation (2) is equal to 2.00 in this case---a value which agrees well with experiment (14). Table III gives K(T) as a function of T over the range of interest in this study (13).

TABLE III

VALUES FOR THE CONSTANT K AT DIFFERENT TEMPERATURES

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

When plotted, this function may be interpolated readily, but extrapolations should be made with some care. The assumptions used in the derivations of the expressions for the intermolecular free length become invalid as the boiling point of the liquid is approached; therefore the normal boiling point of the liquid is the upper limit of applicability of this function. Linear extrapolation below 0°C appears reasonable over modest temperature ranges, but supporting data is lacking.

As mentioned above these relationships are valid for pure substances and mixtures. For mixtures eq. (7) applies

$$L = \frac{2\left[1/\rho - \sum \frac{\omega_i V_{0i}}{M_{0i}}\right]}{\sum \frac{\omega_i Y_i}{M_i}} \qquad (7)$$

Kaulgud (21, 22) has demonstrated that the ultrasonic velocity is largely dependent upon the intermolecular free length (and intermolecular interactions) in binary mixtures of associating and non-associating liquids. Thus is opened the possibility of studying the viscosity of liquid mixtures---its mechanism and correlation---by means of ultrasonic velocity measurements.

In one of his earlier papers Jacobson (16) established the following empirical relation for a wide variety of liquids

$$\phi + C_j = k_j'' \cdot L_\phi M^{-1/2} \tag{8}$$

The free fluidity length is obtained by replacing V_o in equations (3), (4), and (5) by V_ϕ, the molar volume of the subcooled liquid at zero fluidity. This modification seems unnecessary, since all that is required is a consistent basis on which to calculate V_a. V_o is the easier to visualize and admits of more precise calculation. Therefore in this work a correlation will be sought on the basis of L as defined in equation (3) or (5).

The basic purpose behind this work is to evaluate the feasibility of using ultrasonic velocity measurements to study the viscosity and density of mixtures of associating liquids. The goal of this study is a useful preliminary correlation between a simple function of the ultrasonic velocity and the viscosity of liquids and liquid mixtures. To do this the following procedure based on the work of Jacobson (12-18) and Kaulgud (21, 22) will be employed.

Reyburn (33) has shown that the fluidity can be expressed as a simple function of the ultrasonic velocity for mixtures of non-associating liquids. (See Figure 2.) His correlation is of the form

$$\phi = f\left(\frac{K(T)}{u\, M^{1/2}}\right) = k_n\left(\frac{K(T)}{u\, M^{1/2}}\right) + C_n \qquad (9)$$

For associating liquids it is proposed that $M^{\frac{1}{2}}$ be replaced by $(XM)^{\frac{1}{2}}$ where $X = (L_{poly}/L_{mono})^3$ is the degree of association (i. e., the average number of monomers which are clustered together to form a polymeric species). See Figure 1 for schematic definitions of L_{poly} and L_{mono}. It is now left to determine experimentally these two quantities.

The determination of L_{mono} is based on the notion that the thermal expansion of a liquid is independent of the size of the molecular species composing it and the assumption that the degree of association is substantially constant within narrow temperature ranges (10-20°C). Thermal expansion is an intermolecular phenomenon and is related only to the average intermolecular free length in the liquid. Based on this argument and two empirical relationships of wide applicability, Jacobson (17) derives the following equations. (See Appendix A for his derivation.)

$$\rho_o = \rho_T \left[1 + \left(\frac{c}{2}\right) - \left(\frac{c}{2}\right)(1 - T_R)^P\right]^3 \qquad (10)$$

$$L_T = \frac{V_T^{1/3}(2^{1/2}/N)^{1/3}\left[1 - (1 - T_R)^P\right]}{\left[1 + (2/c) - (1 - T_R)^P\right]} \qquad (11)$$

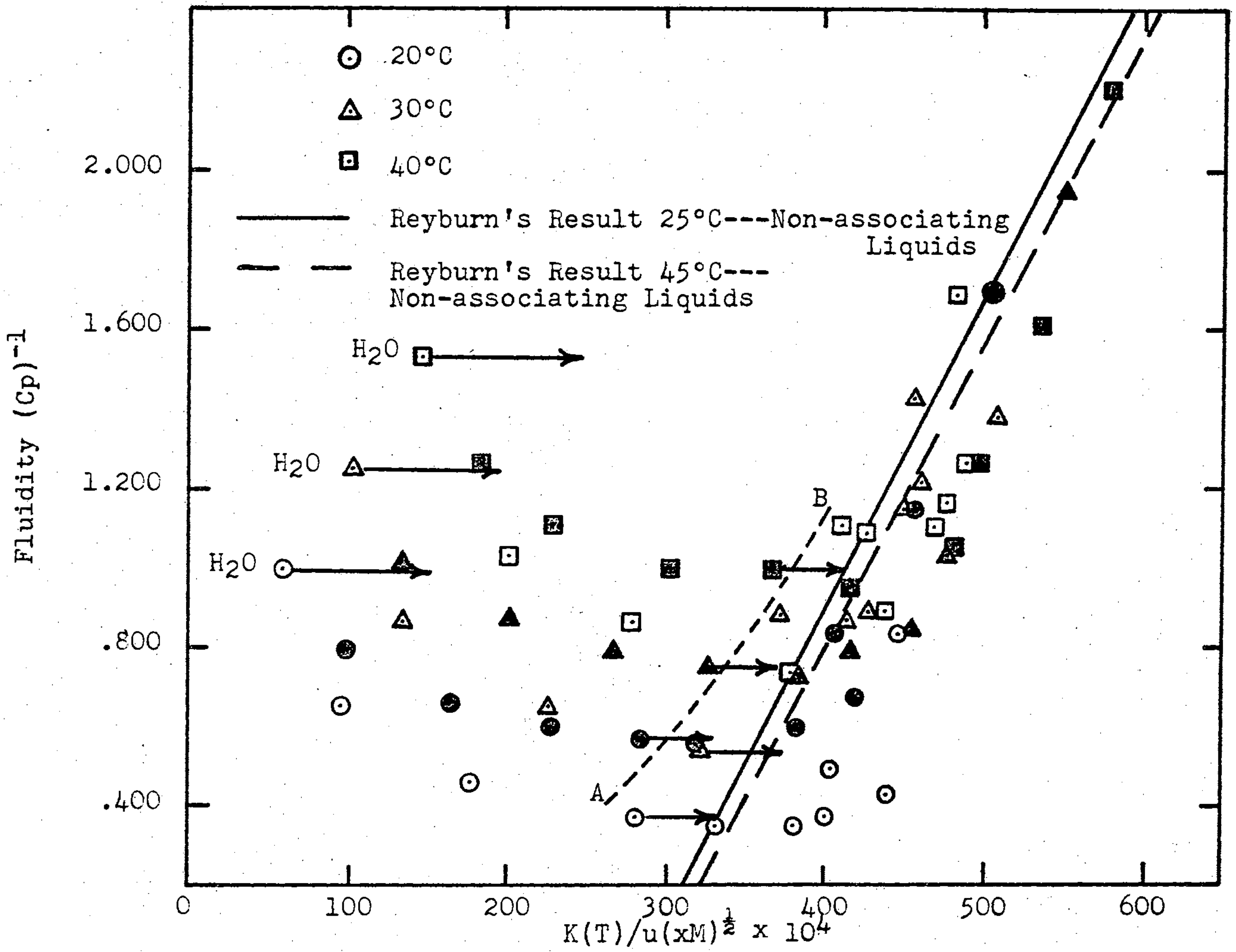


Figure 2. Correlation of Literature Data. Shaded Points are Methyl Alcohol-Water and Unshaded Points are Ethyl Alcohol-Water.

The only data required for the graphical solution of these equations for L_T are the densities of the liquid at two temperatures within 10 or 20°C of one another. (A sample calculation is presented in Appendix C based on graphs constructed for this purpose.) The intermolecular free length determined by this procedure for a liquid composed of associated clusters is the value which would exist in a liquid composed of monomeric species of the same density and temperature as the associated liquid. (See Figure 1.) It should be noted here that a by-product of this procedure is a method of determining quite accurate values of the critical temperatures (or apparent critical temperatures) of mixtures.

The value of L_p can be obtained from either equation (2) or equation (6)---i. e., empirically. It represents the intermolecular free length between the polymeric clusters in the system. (Again, see Appendix C for sample calculations.)

Since

$$L_p = \left(2^{1/2}/N\right)^{1/3} \left(X^{1/3} V_T^{1/3} - X^{1/3} V_0^{1/3}\right)$$

and

~~$L_m = \left(2^{1/2}/N\right)^{1/3} \left(V_T^{1/3} - V_0^{1/3}\right)$~~

~~$X = \left(L_p/L_m\right)^3$~~ ~~(12)~~

Multiplying the molecular weight by this degree of association (at a given temperature) and insertion into Reyburn's correlation for non-associated systems should produce a similar result---i. e., the desired correlation. (See Figure 2.)

For calculating densities and estimating the ultrasonic velocity of mixtures the well-known work of Rao is employed (26, 34). It has been shown that the quantity $Mu^{1/3}/\rho = \overline{R}$ is substantially constant with temperature, and that for binary mixtures

$$\overline{R}_{mix} = x_1 \overline{R}_1 + x_2 \overline{R}_2$$

It is not the purpose of this work to analyze Rao's Rule in any detail; the interested reader may find excellent discussions (and ample references) in the two works cited above. This method was used to estimate the ultrasonic velocities of mixtures of methyl alcohol and toluene; a discussion of the results is given in a later chapter.

CHAPTER V

RESULTS AND DISCUSSION

The Correlation

Reyburn (33) has developed a preliminary correlation between the fluidity and the parameter $K(T)/uM^{\frac{1}{2}}$ as discussed earlier. Development of this function was obtained from measurements on non-associating liquids and liquid mixtures---specifically, mixtures of hexane, cyclohexane, benzene, ethyl benzene, and n-tridecane. These liquids cover a representative range of industrially important compounds, and the initial results are encouraging. The goal of <u>this work</u> is the development of a similar correlation for mixtures of associating liquids.

To achieve the maximum non-idealities (due to large negative excess entropies of mixing) the systems methyl alcohol-water and ethyl alcohol-water were chosen. Both "lattice" and "cluster" type association exist in these mixtures, depending upon the concentration and temperature. Lattice association is in evidence whenever there is a high concentration of water. The water molecule is so constructed that hydrogen bonding (28) is quite extensive, involving degrees of association as high as sixty at 20°C

(18). Cluster association occurs in many substances where (because of steric hindrance and other factors) the degree of association is only of the order of two or three. Carboxylic acids and alcohols exhibit this type of association.

A modification of Reyburn's correlation was attempted by multiplying the molecular weight in his correlating parameter by the degree of association (X). The degree of association is determined as discussed in Chapter IV, and a sample calculation is presented in Appendix C. The results of these calculations are plotted in Figure 2.

There are two classes of data points in Figure 2--- those for which the assumptions of constant degree of association and existence of cluster type association are valid and those for which they are not. The points to the left of line AB have a substantial variation in the degree of association with temperature and lattice type association. (See Table IV for calculated values of X at various temperatures and compositions. These values in general agree well with those cited in Reference 18.) Accurate determination of the degree of association (taking into account its variation with temperature) has shown that many of the errant data points fall into line with those on the right of curve AB. (See arrows in Figure 2.) This is illustrated in the sample calculation of Appendix C. However, those systems with very high concentrations of water still remain well off of Reyburn's lines. Jacobson (18) discusses the

TABLE IV

CALCULATED VALUES FOR PLOTTING FIGURE 2.

Methyl Alcohol-Water

Weight % Alcohol (38)	ϕ(20°C)	x(20°C)	$\frac{K(20°C)}{u(xM)^{1/2}}$	ϕ(30°C)	x(30°C)	$\frac{K(30°C)}{u(xM)^{1/2}}$	ϕ(40°C)	x(40°C)	$\frac{K(40°C)}{u(xM)^{1/2}}$
0	0.9950	290.0	0.0058	1.2489	93.0	0.0102	1.5291	44.0	0.0147
10	0.7981	88.0	0.0099	1.0183	49.0	0.0134	1.2610	26.0	0.0185
20	0.6596	29.0	0.0164	0.8734	20.0	0.0202	1.1086	16.0	0.0230
30	0.5952	14.2	0.0227	0.7955	10.9	0.0267	1.0111	8.9	0.0304
40	0.5650	8.9	0.0283	0.7524	7.2	0.0328	0.9970	6.0	0.0369
50	0.5562	7.1	0.0319	0.7337	5.3	0.0385	0.9569	4.8	0.0416
60	0.5949	5.1	0.0382	0.7880	4.6	0.0418	1.0030	4.4	0.0444
70	0.6609	4.4	0.0419	0.8446	4.1	0.0456	1.0571	3.9	0.0482
80	0.8389	5.0	0.0406	1.0373	3.9	0.0477	1.2755	3.9	0.0499
90	1.1442	4.2	0.0456	1.3774	3.7	0.0509	1.6129	3.6	0.0537
100	1.6920	3.7	0.0505	1.9417	3.4	0.0552	2.2173	3.4	0.0580

Ethyl Alcohol-Water

Weight % Alcohol (38)	ϕ(20°C)	x(20°C)	$\frac{K(20°C)}{u(xM)^{1/2}}$	ϕ(30°C)	x(30°C)	$\frac{K(30°C)}{u(xM)^{1/2}}$	ϕ(40°C)	x(40°C)	$\frac{K(40°C)}{u(xM)^{1/2}}$
0	0.9950	290.0	0.0058	1.2489	93.0	0.0102	1.5291	44.0	0.0147
10	0.6502	91.0	0.0095	0.8621	46.0	0.0135	1.0309	21.0	0.0202
20	0.4581	23.0	0.0177	0.6439	14.6	0.0226	0.8621	9.9	0.0280
30	0.3690	8.3	0.0281	0.5348	6.8	0.0323	0.7310	5.8	0.0380
40	0.3436	5.7	0.0339	0.8834	5.1	0.0373	1.1198	4.5	0.0411
50	0.3484	4.0	0.0381	0.8658	4.2	0.0413	1.0953	4.2	0.0428
60	0.3745	4.1	0.0401	0.8873	3.9	0.0428	1.1086	3.5	0.0470
70	0.4219	3.4	0.0438	0.9416	3.5	0.0452	1.1682	3.4	0.0477
80	0.4980	3.2	0.0403	1.0331	3.3	0.0462	1.2674	3.2	0.0490
100	0.8333	3.0	0.0446	1.4245	3.2	0.0456	1.6892	3.1	0.0473

reason for this.

> ...the concept of free length has no significance when the molecules are bound together with highly directional forces similar to those in the solid state. However, with rising temperature the lattice order is reduced and the system gets more like that of an ordinary liquid.

As mentioned earlier, water is a "lattice" associated liquid, and as such cannot be expected to obey this theory (at least at temperatures much below 50°C). For instance, the value of X determined by the method of this work is 290, whereas the accepted value is about 60 (18). The systems chosen for the demonstration of the validity of this approach therefore present its severest test.

Taking into account variations in degree of association and the existence of lattice type association causes the points to agree well with Reyburn's on normal mixtures. The amount of scatter is also comparable, and the results are shown in Figure 2. Since these data are from a number of sources (density and ultrasonic velocity from Reference 26 and viscosity from Reference 38), a rough quantitative analysis is all that can be justified. All points were compared with Reyburn's results (on data from a single source) at 25°C and 45°C. The absolute mean deviation of all points to the right of line AB is about 25% at 45°C and about 23% at 25°C. (See Appendix A for a breakdown and discussion of this error analysis.) No attempt was made to separate the points according to temperature, because the scatter is comparable at all three temperatures.

Since this scatter appears to be random rather than systematic, these results support the basic tenets of this technique. Therefore, the recommendation that more single source data (density, viscosity, and ultrasonic velocity) be taken on a variety of associating systems is suggested.

It is the opinion of this author that modifying the original definition of the intermolecular free length by determining (1) the amount of deviation from sphericity of the molecular species and associated clusters in the mixtures and (2) the type of packing and orientation of the species would correct some of the severe deviations. See references 21 and 24 for preliminary studies on this point. Here a possible approach based on these works will be outlined briefly; much more data is required before any useful generalizations can be made.

The form factor is defined (21)

$$f = \frac{\text{actual surface area of the molecules}}{\text{spherical surface area inclosing same volume}}$$

where the surface area of a molecule is visualized as that of its electron cloud. Some way must be found of estimating the shape of the molecular species taking part in the physical phenomena of interest here. Eyring (24) has presented a significant work along these lines for hydrocarbon molecules. Depending on the temperature range in which the liquid is in, the molecules may be visualized as occupying rectangular volumes (low temperatures) or cylindrical volumes (higher temperatures where the molecules rotate about their long axis). Based upon interatomic distances in molecules, the volumes and surface areas (based upon these volumes) can be calculated and compared with the surface areas of spheres of the same volumes---leading to a formal calculation of the form factors. Average form factors (based upon mole fractions) can also be determined for mixtures. Interatomic distances are available (see for example, Reference 28), and the introduction of subsequently calculated form factors have been partially successful in modifying the correlation. Kaulgud (21) determined experimental values of form factors ranging from about 0.90 to 1.07. A look at Figure 2 will show the reader that numbers in this range will correct the abscissa $K(T)/u(xM)^{\frac{1}{2}}$ of many of the points---i. e., multiplying it by f.

When applying this procedure to the results of this study, success and failure occurred with equal frequency. The opinion of this author is that the complexities of the interactions of electron clouds must be investigated further before the theory of form factors can be made useful.

This work has shown that the viscosity of liquids can be correlated by a simple function of the ultrasonic velocity. Although the accuracy still leaves something to be desired, the trend is correct and more work is definitely recommended.

Molecular Arguments

The excess entropy is the most important thermodynamic function used in the qualitative analysis of ultrasonic velocity-composition curves (22) and viscosity-composition curves. Supplementary data on the degree of association in liquids as a function of temperature and composition is also useful in developing insight into the molecular natures of transport phenomena and sound transmission. The related effects of changes in (1) density with composition and temperature, (2) excess heat of mixing with composition, (3) intermolecular free length with composition and temperature, and (4) external pressure can be of considerable importance in special systems and environments. The interrelations among these effects often result in rather unusual and unexpected behavior. These notions will now be explored in terms of a few specific illustrations.

Ethyl Alcohol and Water

Figures 6 through 10 show the viscosity, density, and ultrasonic velocity versus composition curves for this system at several temperatures throughout the liquid range and at atmospheric pressure. There are maxima in all of the ultrasonic velocity and viscosity curves along with slight negative deviations in the density curves. Figure 11 gives a qualitative picture of the excess thermodynamic functions for this system (33). From these graphs certain deductions

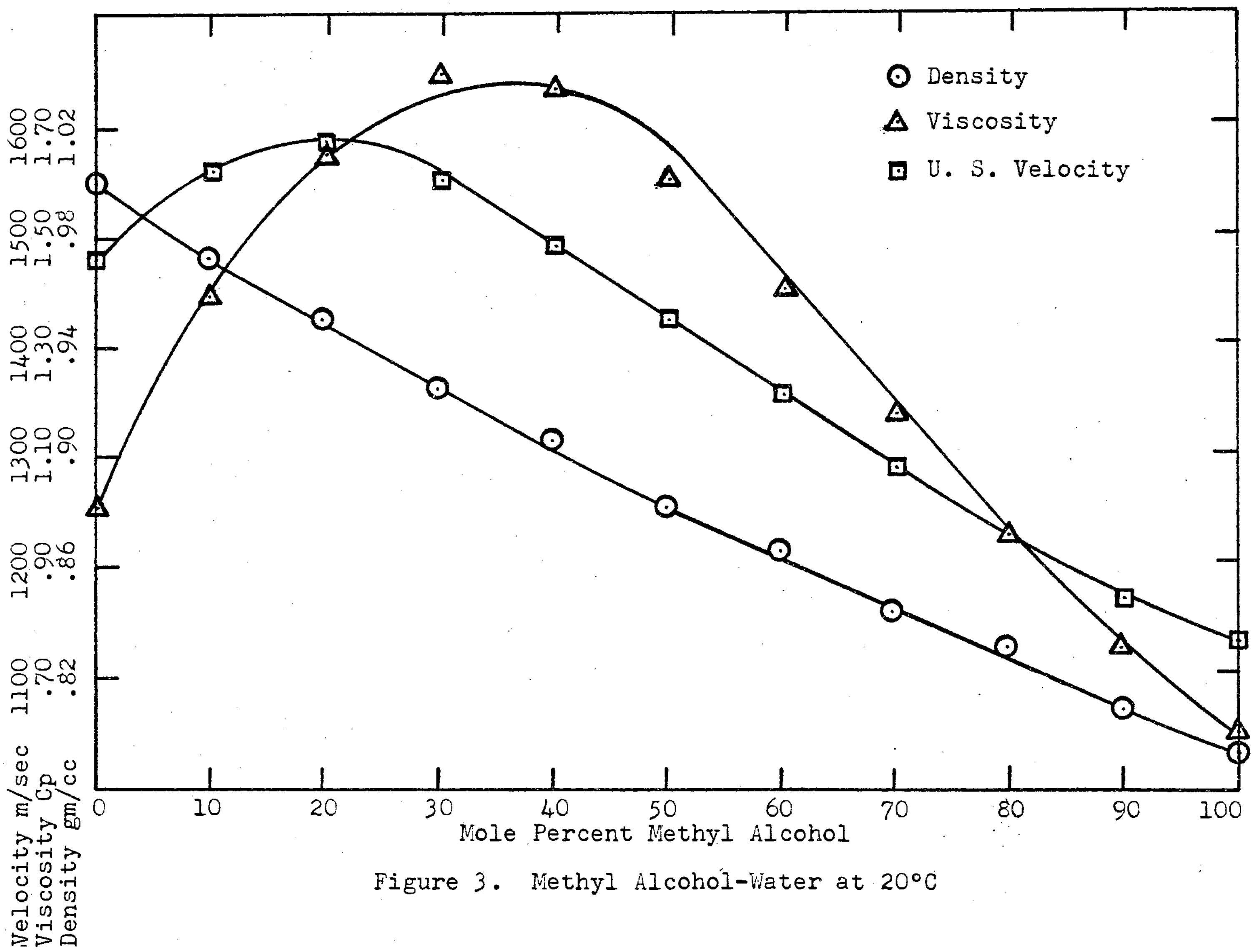


Figure 3. Methyl Alcohol-Water at 20°C

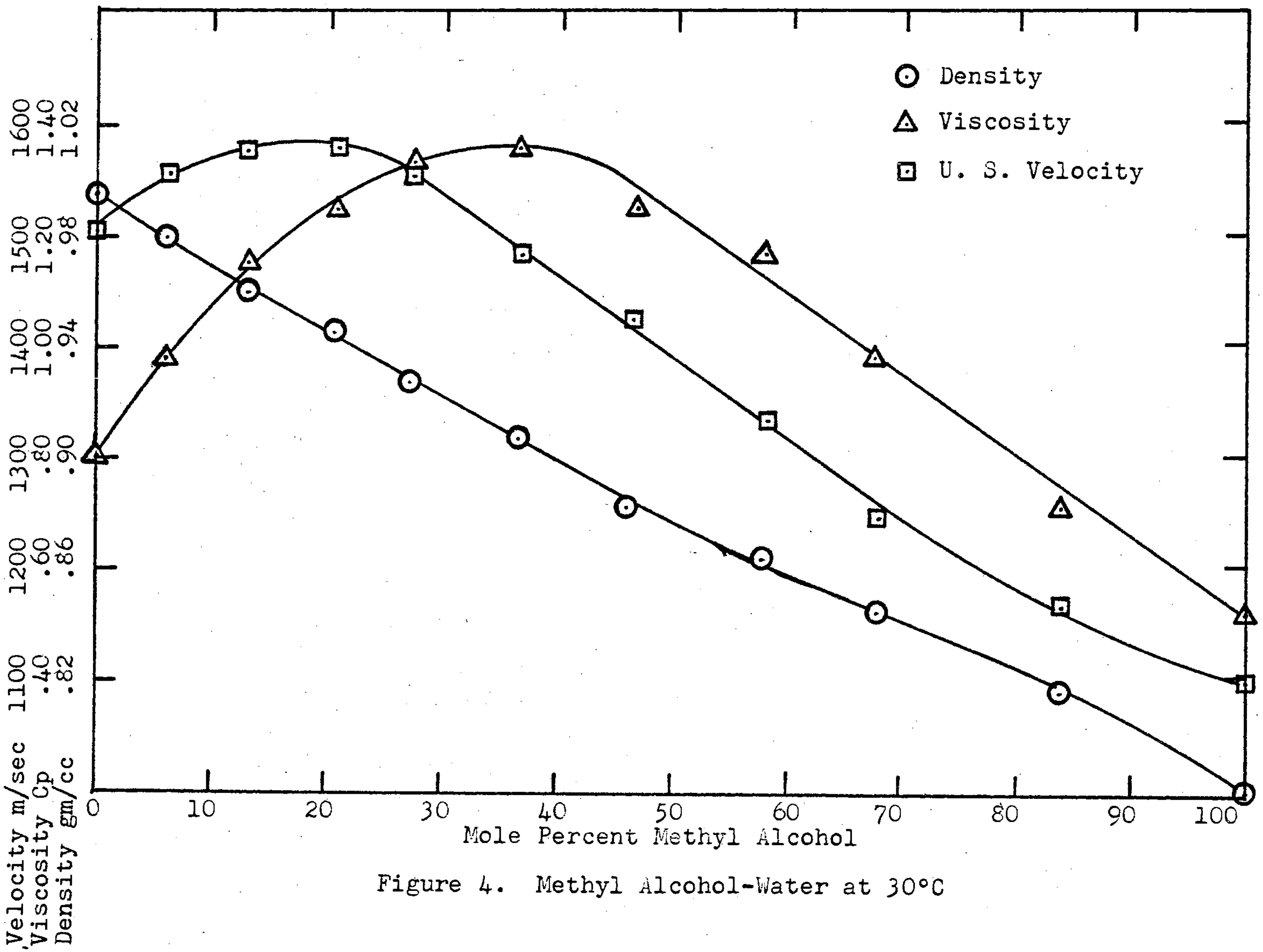


Figure 4. Methyl Alcohol-Water at 30°C

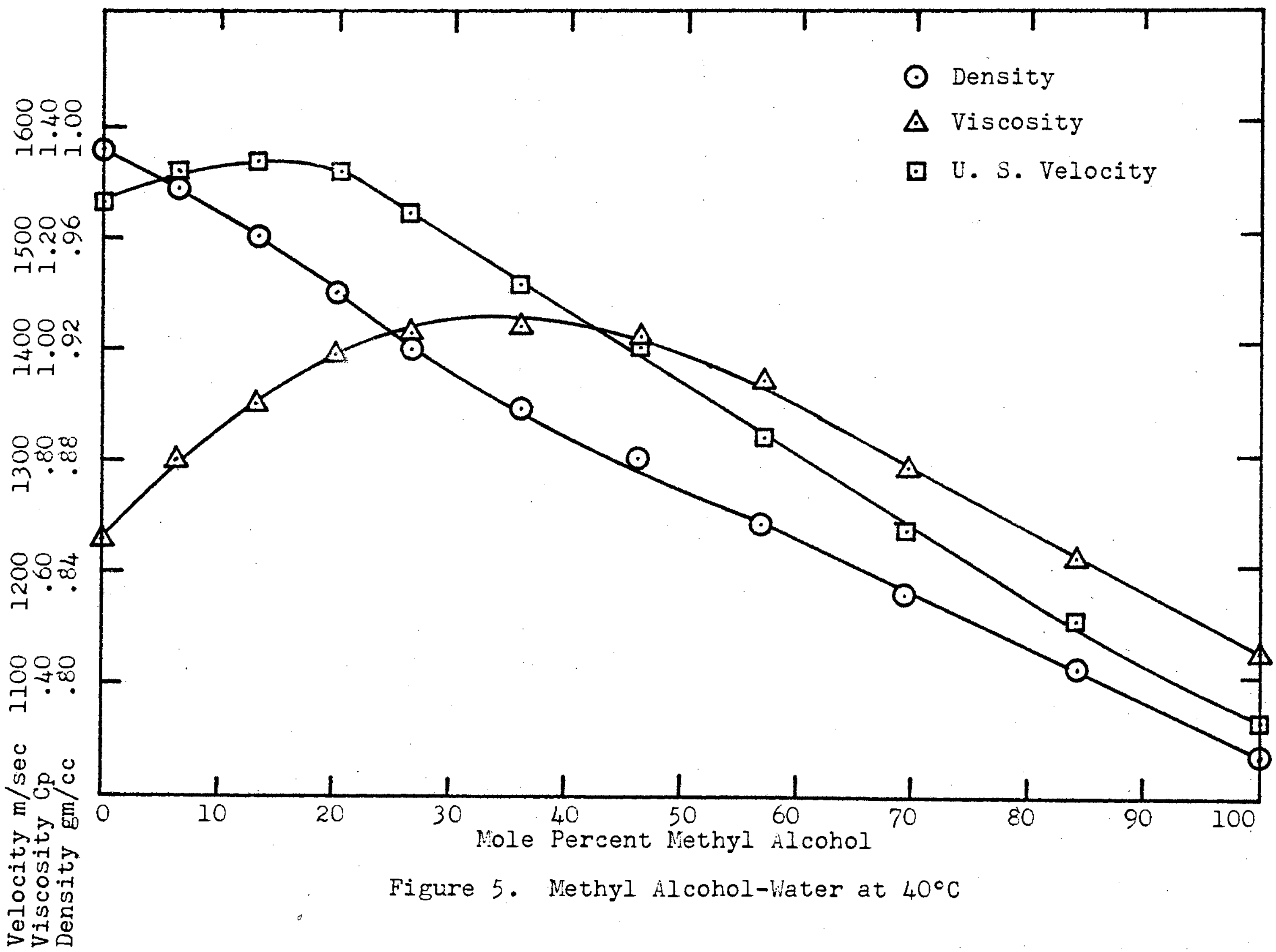


Figure 5. Methyl Alcohol-Water at 40°C

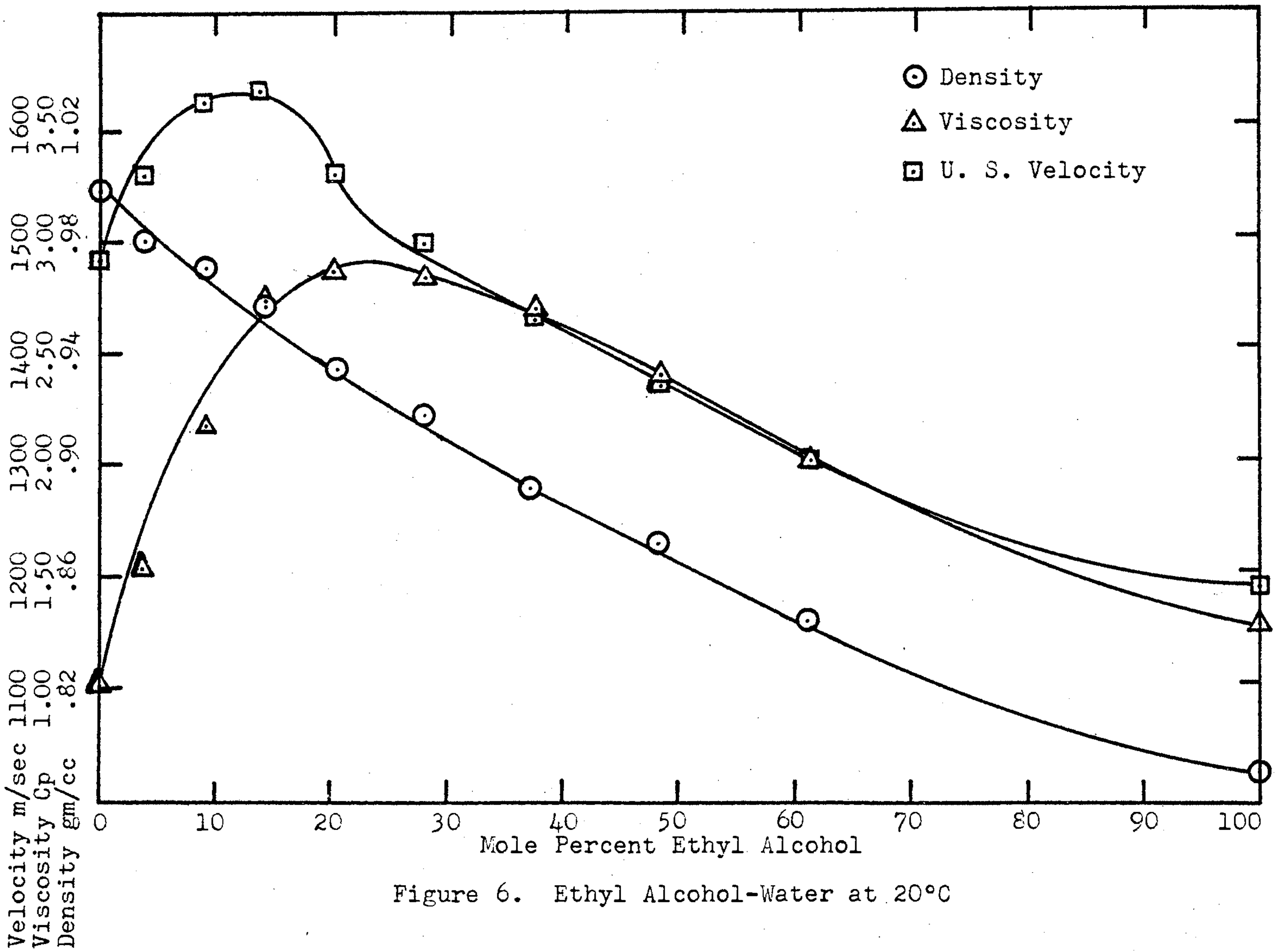


Figure 6. Ethyl Alcohol-Water at 20°C

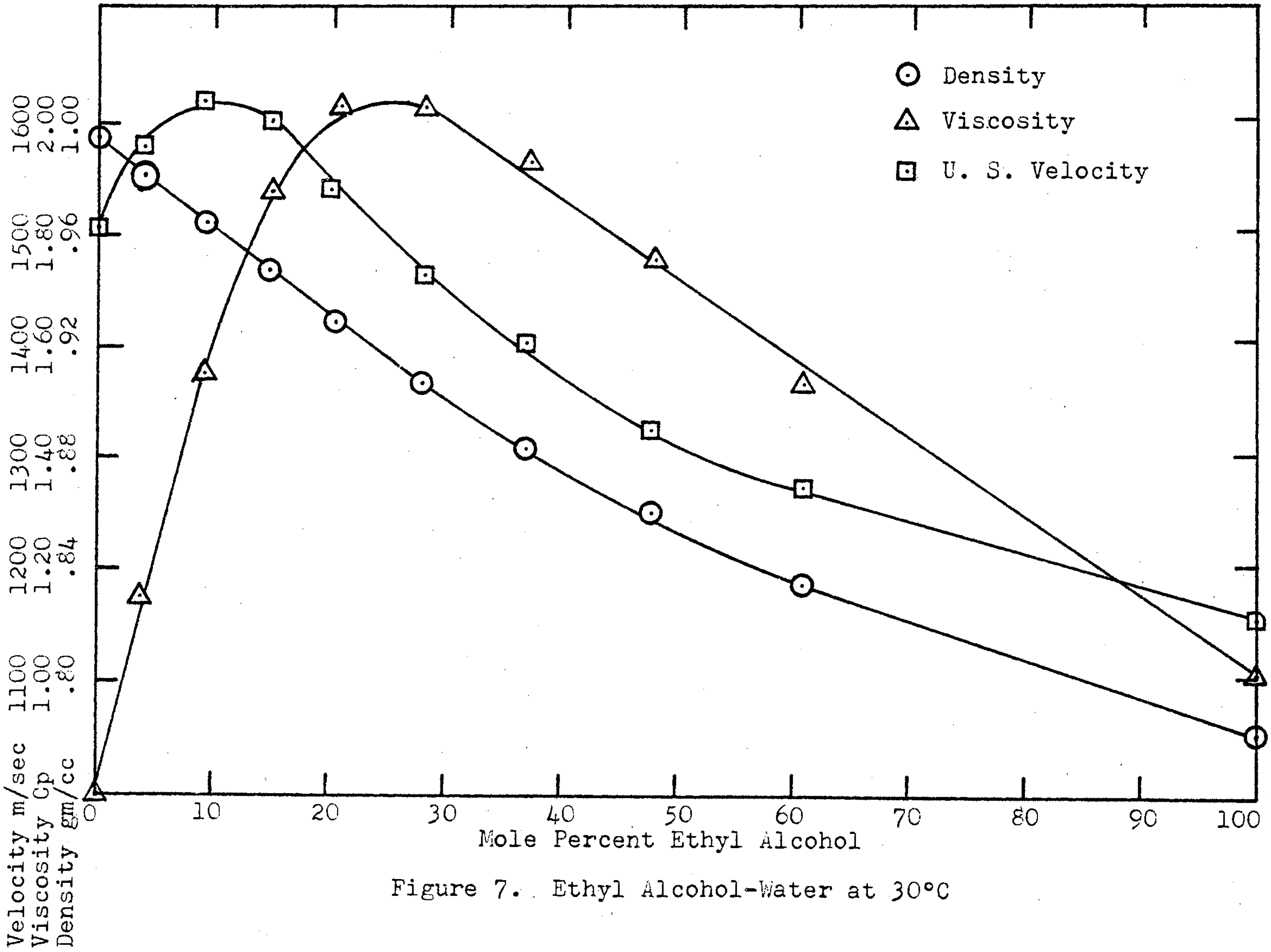


Figure 7. Ethyl Alcohol-Water at 30°C

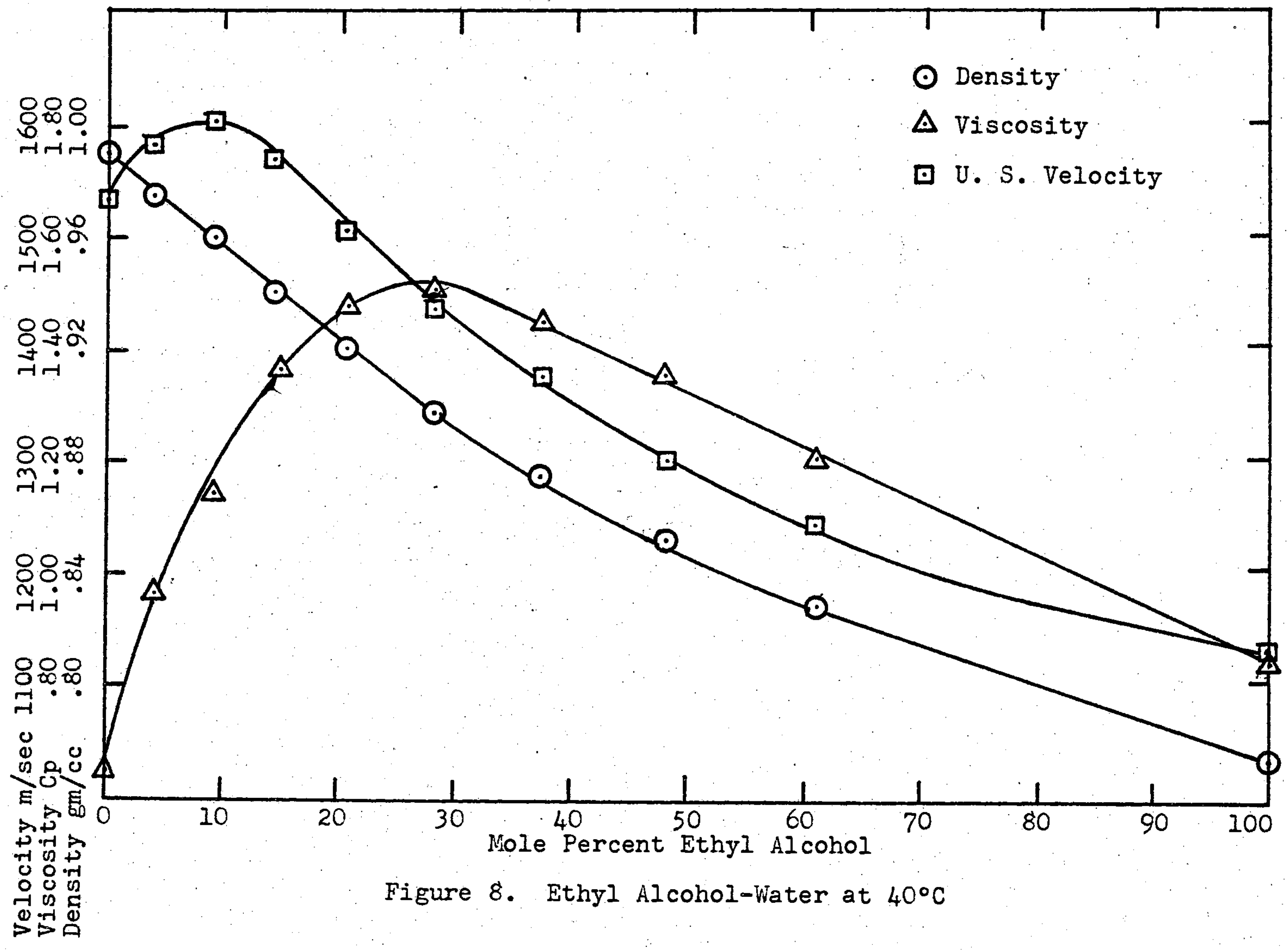


Figure 8. Ethyl Alcohol-Water at 40°C

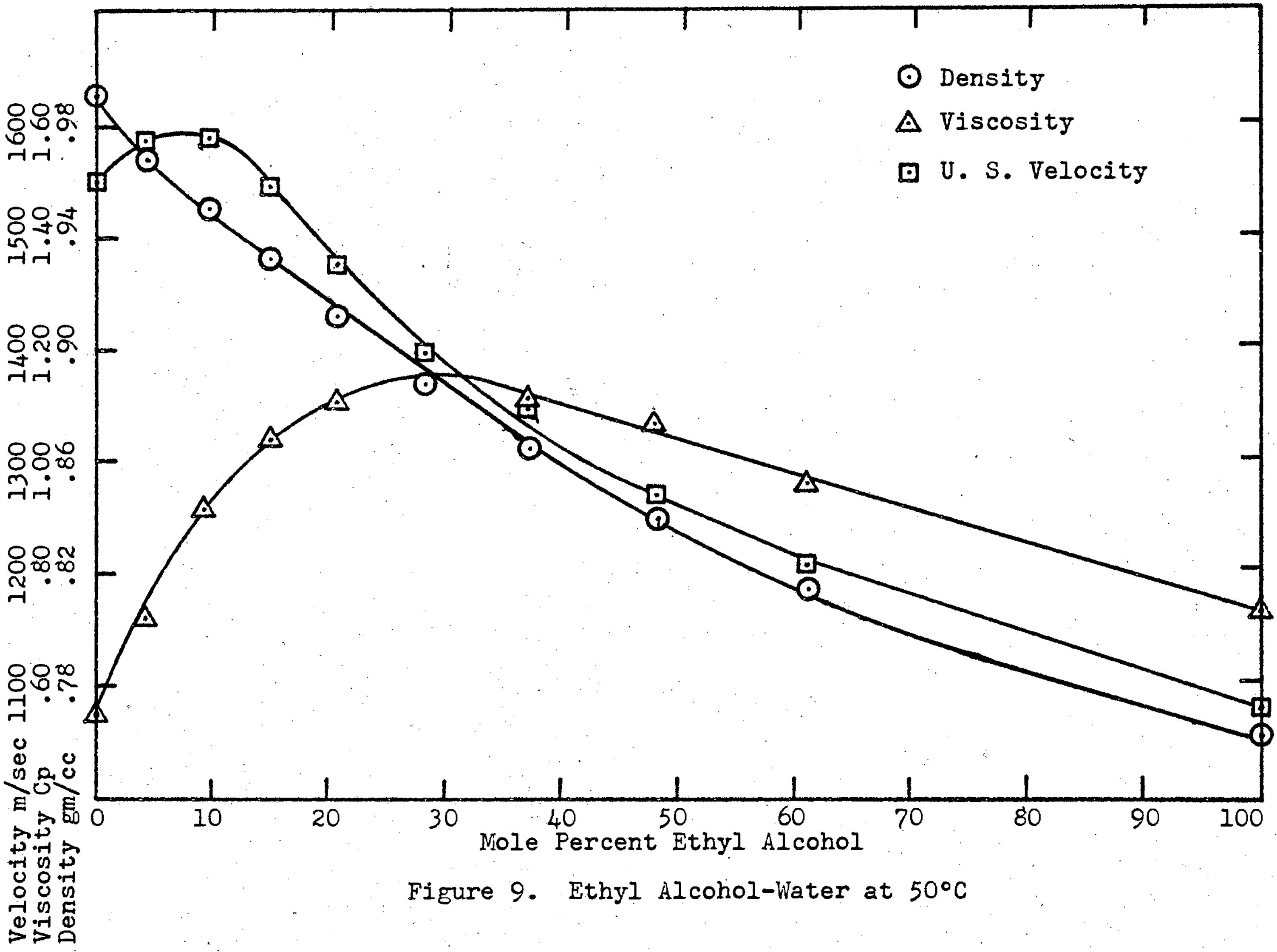


Figure 9. Ethyl Alcohol-Water at 50°C

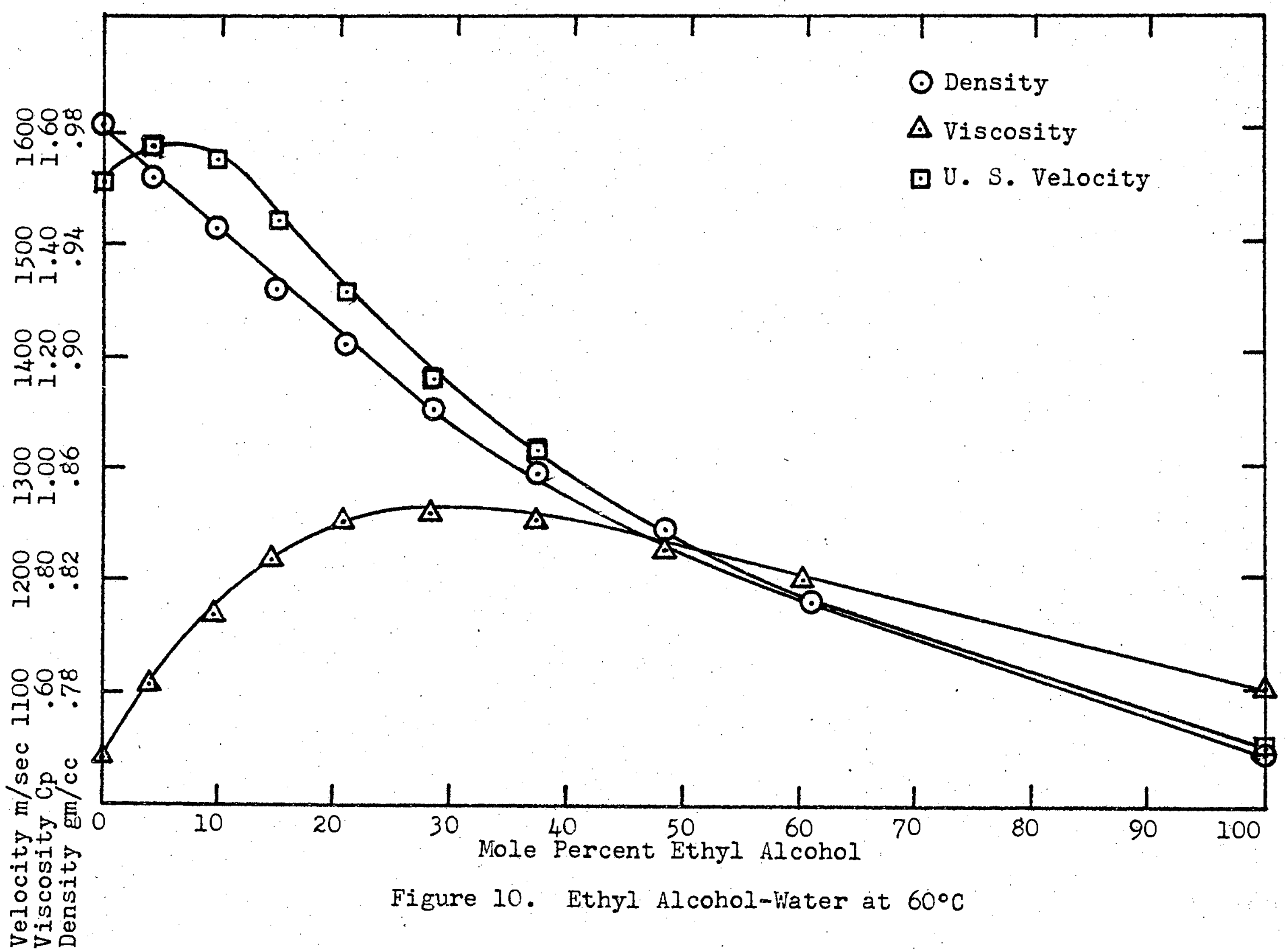


Figure 10. Ethyl Alcohol-Water at 60°C

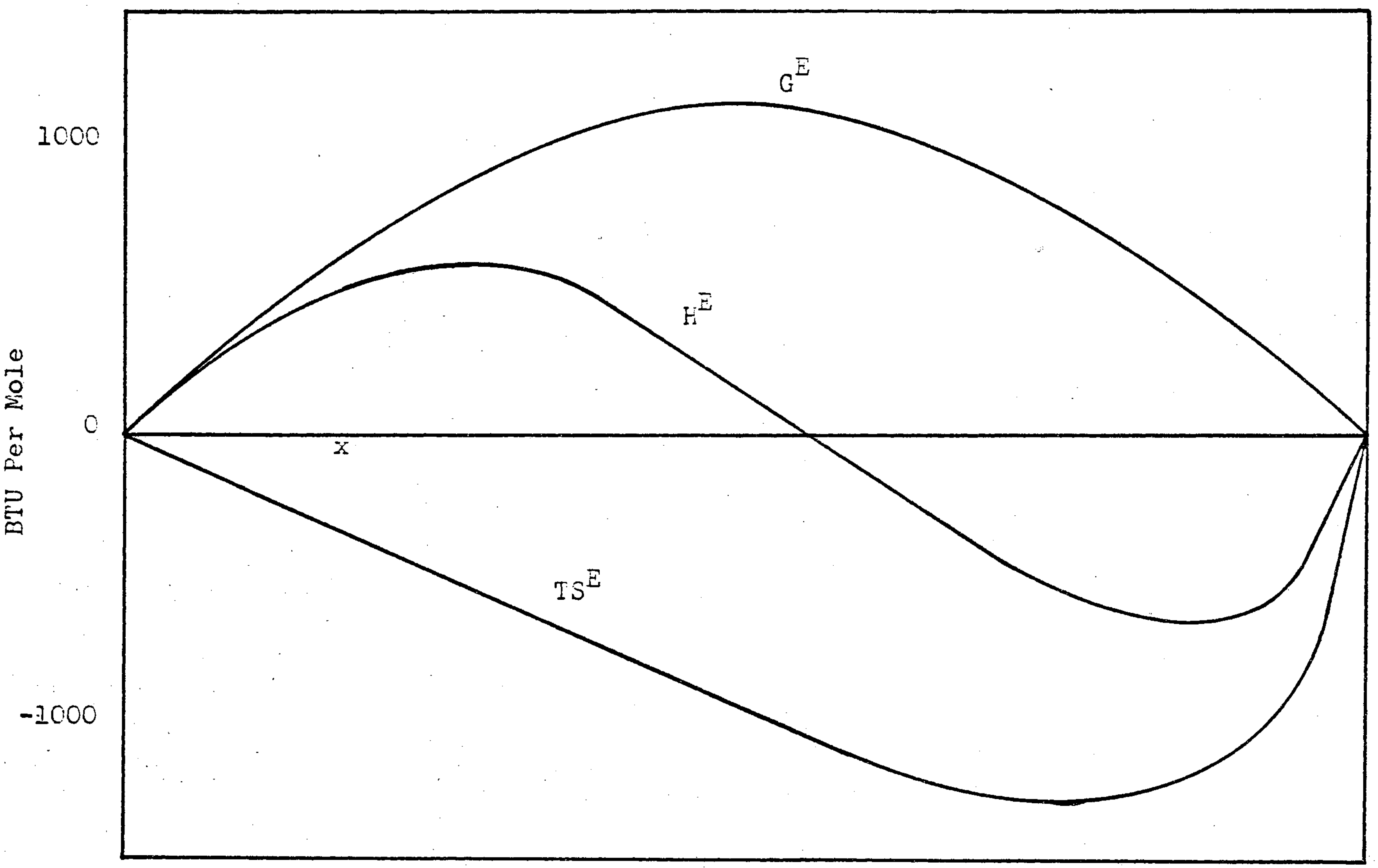


Figure 11. The Excess Functions of Water + Ethyl Alcohol (Above Room Temperature) as a Function of Mole Fraction Water (33)

can be made respecting the detail (at the molecular level) behind these variations in the macroscopic properties with composition and temperature.

As small amounts of water are added to ethyl alcohol, the lattice associated structure of the water is broken down. This is evidenced by the positive excess heat of mixing (hydrogen bond breakdown). The negative excess entropy illustrates that there is nevertheless a considerable degree of association still extant in the mixture. At higher concentrations of water more and more of the lattice structure of the water survives the mixing process; and, at very high water concentrations, the ethyl alcohol molecules are essentially incorporated into the lattice type structure. The negative excess heats of mixing (hydrogen bond formation) and large negative excess entropies give the clue to this effect.

The intermolecular free length versus composition curves exhibit minima---anti-parallel to the viscosity and ultrasonic velocity curves. These intermolecular free length curves are a result of the combined effects of different sized molecules and varying degrees of association.

These results allow the following interpretation of the ultrasonic velocity and viscosity curves. Lattice structures and non-associated systems transmit sound more readily than cluster associated systems. The lattice structures are good sound transmitters because of their relatively rigid makeup, whereas the non-associated systems (also good sound carriers) in general have small intermolecular free lengths. Cluster associated systems have lower sound transmitting ability because of their larger intermolecular free lengths. (See Figure 1.) From this and the excess function curves the ultrasonic velocity-composition graphs are explained.

To explain the viscosity-composition curves it must be realized that the associated complexes must be broken down by the flow process. Since hydrogen bonds possess a relatively high energy (2-10 kcal. per mole), it is evident that the activation energy for flow (4, 23) must be greater than for comparable non-associated systems. On the basis of Friend's (6) model for momentum transport the intermolecular free length should also play a role in determining the viscosity---e. g., small intermolecular free lengths mean high intermolecular forces and consequent high viscosity. Combining these effects for associated systems leads to an explanation of the viscosity-composition curves.

Similar reasoning can be applied to explain the behavior of the methyl alcohol-water system.

The systems benzene-ethyl alcohol (Figure 13) and ethyl alcohol-ethyl benzene (Figure 12) appear to contradict what has been said earlier---their viscosity decreases with increasing benzene concentration whereas their ultrasonic velocity increases with benzene concentration. However, by combining excess function (33) and molecular configuration

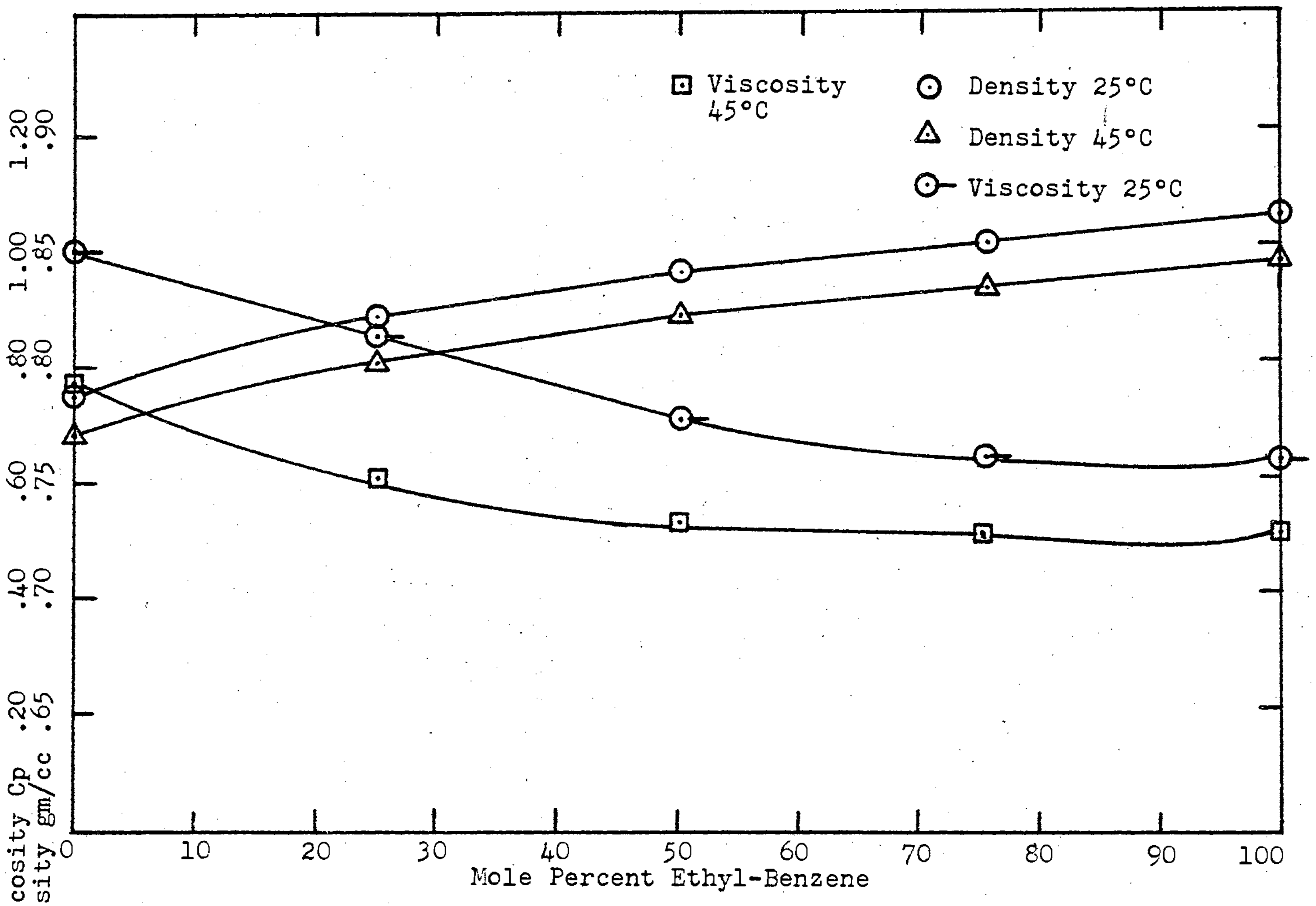


Figure 12. Ethyl Benzene-Ethyl Alcohol

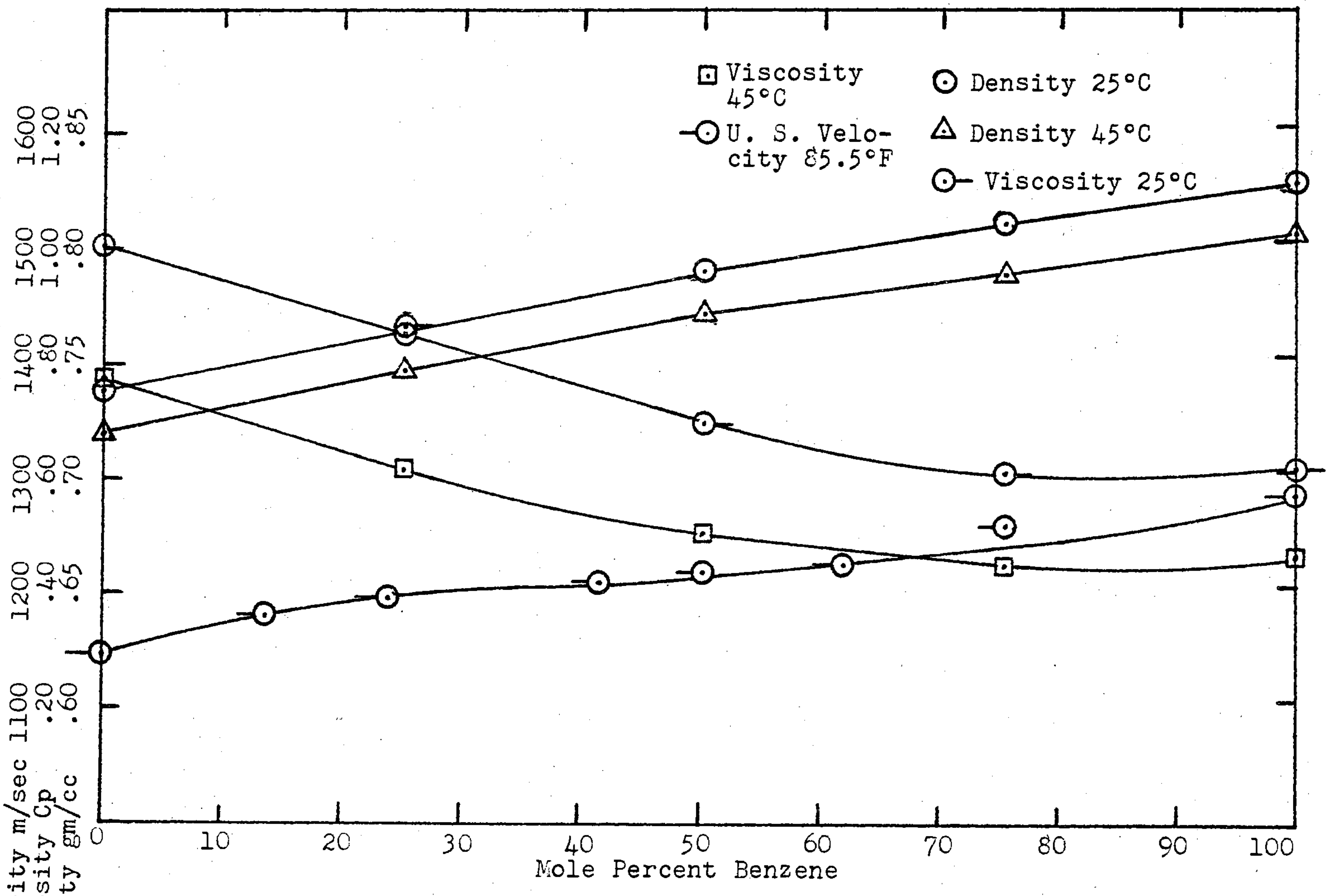


Figure 13. Benzene-Ethyl Alcohol

arguments this behavior can also be explained. For instance, at high concentrations of benzene most of the association has been destroyed by the high aromaticity (10). Therefore the ultrasonic velocity is high, as breakdown of association complexes usually results in a smaller average intermolecular free length in the liquid. But the viscosity is becoming smaller at these high concentrations, contrary to what would be expected on a purely intermolecular forces argument. This is explained by observing that in this case more energy is required to breakdown the association complexes at low benzene concentrations and then produce activation for flow than is required for simple activation of the monomers at high benzene concentrations. Benzene, being a planar species, tends to have less difficulty arranging itself in flow laminae.

The system toluene-methyl alcohol (Figure 14) presents the maximum degree of non-ideality in its viscosity-composition curve; i. e., a maximum and a minimum. Although no ultrasonic velocity data have been located for this system, Rao's Rule (26) has been applied to obtain an estimate of the ultrasonic velocity-composition curve. Rao's constant was calculated for each pure component (the ultrasonic velocity data are available for methyl alcohol and toluene), and the formula

$$\bar{R}_{mix} = x_1 \bar{R}_1 + x_2 \bar{R}_2$$

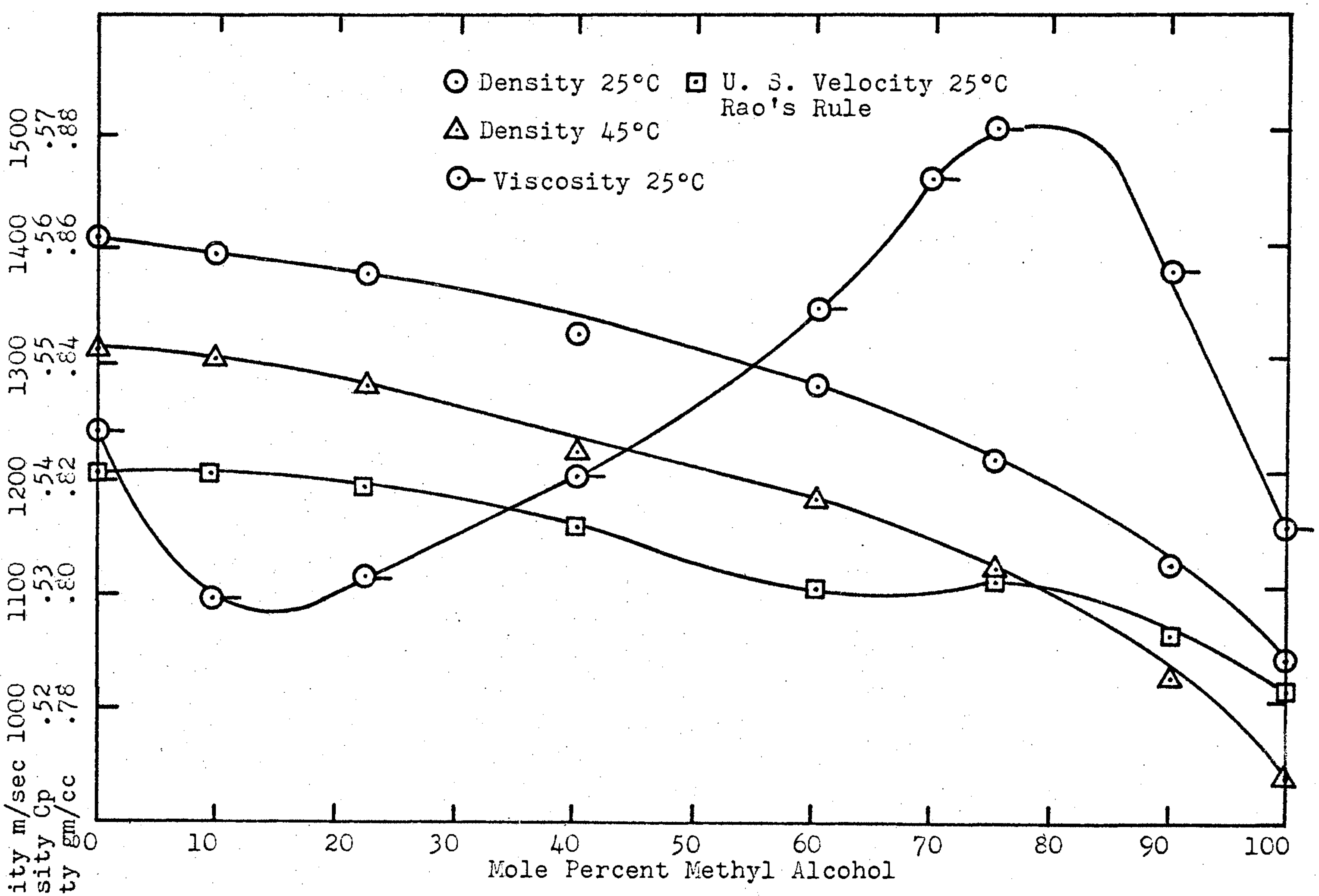


Figure 14. Toluene-Methyl Alcohol

was used to calculate the ultrasonic velocity of the mixtures. On the basis of this and excess function plots (33), it appears that this behavior can also be described in terms of molecular considerations in a manner similar to the above cases. It is recommended that careful ultrasonic velocity measurements be made on this system.

In the recent valuable work by Rowlinson (33) a number of specific binary systems are discussed, and the general nature of mixtures of associating liquids is well presented along with ample references to the literature.

The foregoing discussion unveils the possibility of using ultrasonic measurements to study the excess thermodynamic functions of liquid mixtures---with the prediction of liquid activity coefficients as a foreseeable reward, since the activity coefficient is directly related to the excess free energy.

Group Interactions and Group Solutions

Two rather general models for describing intermolecular interactions in liquids in a semi-empirical manner have been developed in recent years. Pierotti and his coworkers (29, 30, 31) visualize group interactions (i. e., "contacts" between the substituted radicals on molecular species) as the determinants of the physical properties of the liquid or liquid mixture. These interactions are viewed as occurring in pairs---e. g., an interaction between a phenyl group (or radical) and an hydroxyl group or between a methyl group and an aldehyde group. The key point is that these group interactions are the same irrespective of the molecular makeup of the liquid, so that data taken on one system containing certain groups is valid for other systems containing these same groups. Wilson and others (37, 39) have visualized a liquid or liquid mixture as a solution of groups (or radicals), rather than as a solution of molecules. Each group contributes a certain amount to each physical property, depending upon (1) the atoms which compose it, (2) its shape and structural characteristics, and (3) its concentration (group fraction) in the solution. As yet these approaches have been applied only to the prediction of liquid phase activity coefficients and the heat of mixing, but there is no conceptual difficulty involved in extending their usefulness to other physical properties.

The *a priori* prediction of degrees of association would be a possible application of this approach. From an analysis of the phenomenon of hydrogen bonding (10, 28), two factors crop up as vital to its understanding. These are (1) the nature of the polar groups present in the liquid (i. e., the atoms involved) and (2) the steric situation in the molecules (e. g., how accessible to a "bare proton" is the electronegative atom to which it is attempting to bond). Highly electronegative atoms, such as fluorine and oxygen, are good prospects for hydrogen bonding from a purely chemical standpoint; and ideally formed molecules, such as water, are ideally suited for hydrogen bonding from a steric viewpoint. Addition to the molecules of complex, non-polar substrates tends to inhibit association by making the negative centers of attraction relatively inaccessible.

When these principles were applied to the methyl alcohol-water and ethyl alcohol-water systems, it was found that very little steric information could be obtained. However, a good analysis of the O-H---O bond was developed. (See Table IV for the variation of X with composition.) A plot was made of X (degree of association) versus group fraction of the polar group (-OH), water (pure) being assumed equal to 1.6 hydroxyl groups (37). The result was a smooth plot which could be used to predict the degree of association containing only methyl groups ($-CH_3$) and hydroxyl groups. With the accumulation of more data on a variety of systems, it should be possible to develop generalized equations involving both the steric and type contributions similar to Pierotti's correlation for the heat of mixing in non-associating systems. He has stated (31)

> ...a model of the nature of the present one cannot comprise the formation of complexes or association. But there is no obstacle to combining group interaction results and relations obtained from a theory of association.

CHAPTER VI

SUMMARY

The results of this study indicate that there exists a general relationship between the viscosity and ultrasonic velocity in associating liquids. That this should be so is evident from the fact that both ultrasonic transmission and momentum transport depend upon the intermolecular free length in a liquid. Other liquid state phenomena and liquid thermodynamic properties have also been shown to be related to the ultrasonic velocity. As yet quantitative precision is lacking, but it is the author's opinion that this is due primarily to the use of literature data in developing the correlation and not to defects in the theory.

Recommendations

(1) Careful measurements should be carried out on the system methyl alcohol-toluene (ultrasonic velocity, viscosity and density), because both a maximum and a minimum occur in the viscosity versus composition curve. Thus the range of solution non-idealities could be covered with one set of measurements.

(2) The liquids studied should be investigated throughout their ranges of existence---i. e., from the

melting point to the critical point. The nature of the liquid state would thereby be illuminated in much greater detail.

(3) Other polar groups should be investigated---e. g., acids and aldehydes---for different strength and structural effects. This would lead to group contribution relationships for the various properties.

(4) Ultrasonic velocity measurements could be used to follow the progress of liquid phase chemical reactions which result in a marked change in the intermolecular free length and/or degree of association. Thus it promises to be a valuable tool in kinetic studies.

(5) Research workers should design and build their own apparatus to be used in future studies. The advisability of this tack is emphasized by the comments in References 22 and 26.

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APPENDIX A

In this section the basic equations used to determine the degree of association in pure liquids and liquid mixtures will be derived. These relationships will then be used to demonstrate the calculational procedures involved (Appendix C). The method is due to Jacobson and Heedman (17, 18).

For a system composed of spherical molecules in hexagonal close packing

$$L_T = \left(\frac{2^{1/2}}{N}\right)^{1/3} \left(V_T^{\ 1/3} - V_0^{\ 1/3}\right) \tag{13}$$

and the radius of these spherical molecules is

$$r_0 = \frac{1}{2}\left(\frac{2^{1/2}}{N}\right)^{1/3} V_0^{\ 1/3} \tag{14}$$

Equations (13) and (14) are derived from simple geometric considerations (7).

Jacobson (17) now invokes an empirical relationship of rather wide generality, i. e.,

$$\frac{\rho_0}{\rho_c} = 3.75 \tag{15}$$

These three expressions combine to give

$$L_c = C r_0 \tag{16}$$

At this point the second of the empirical equations is presented.

$$(1 - L_R) = (1 - T_R)^p \tag{17}$$

This expression is based on the Theorem of Corresponding States applied to L.

Combination of all five of these relations gives

$$\rho_o = \rho_T \left[1 + \left(\frac{C}{2}\right) - \left(\frac{C}{2}\right)(1 - T_R)^p\right]^3 \tag{18}$$

The constants were determined experimentally and found to be

$$c = 1.092$$

$$p = \frac{1}{4}$$

for a variety of substances (17). If the density of a liquid or liquid mixture is known at two temperatures, the critical temperature can be found from equation (18). Figure 15 is the graph which is used for this purpose. Graphs similar to Figure 15 have been constructed for a number of density ratios.

From equations (14, (17), and (18) is derived equation (19).

$$\frac{L_T}{V_T^{1/3}} = \frac{(2^{1/2}/N)^{1/3}\left[1 - (1 - T_R)^p\right]}{\left[1 + (2/c) - (1 - T_R)^p\right]} \tag{19}$$

Figure 16 shows the graphical solution technique used on this expression. L_T is then obtained by multiplying by

$$V_T^{1/3} = \left(\frac{M}{\rho_T}\right)^{1/3}$$

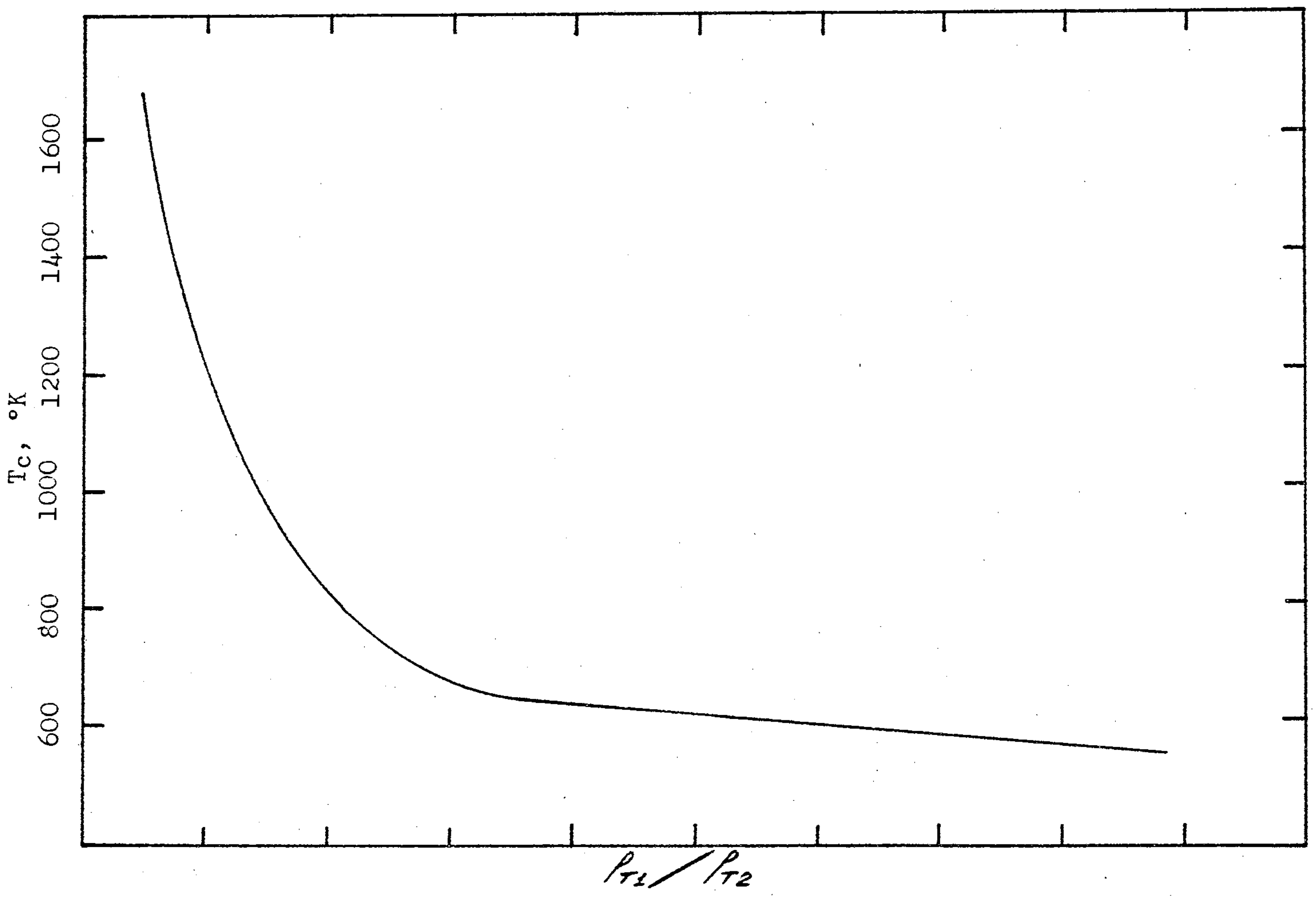

Figure 15. Critical Temperature vs Density Ratio. The Exact Shape of the Curve and Values of the Abscissa Depend Upon the Temperature Range.

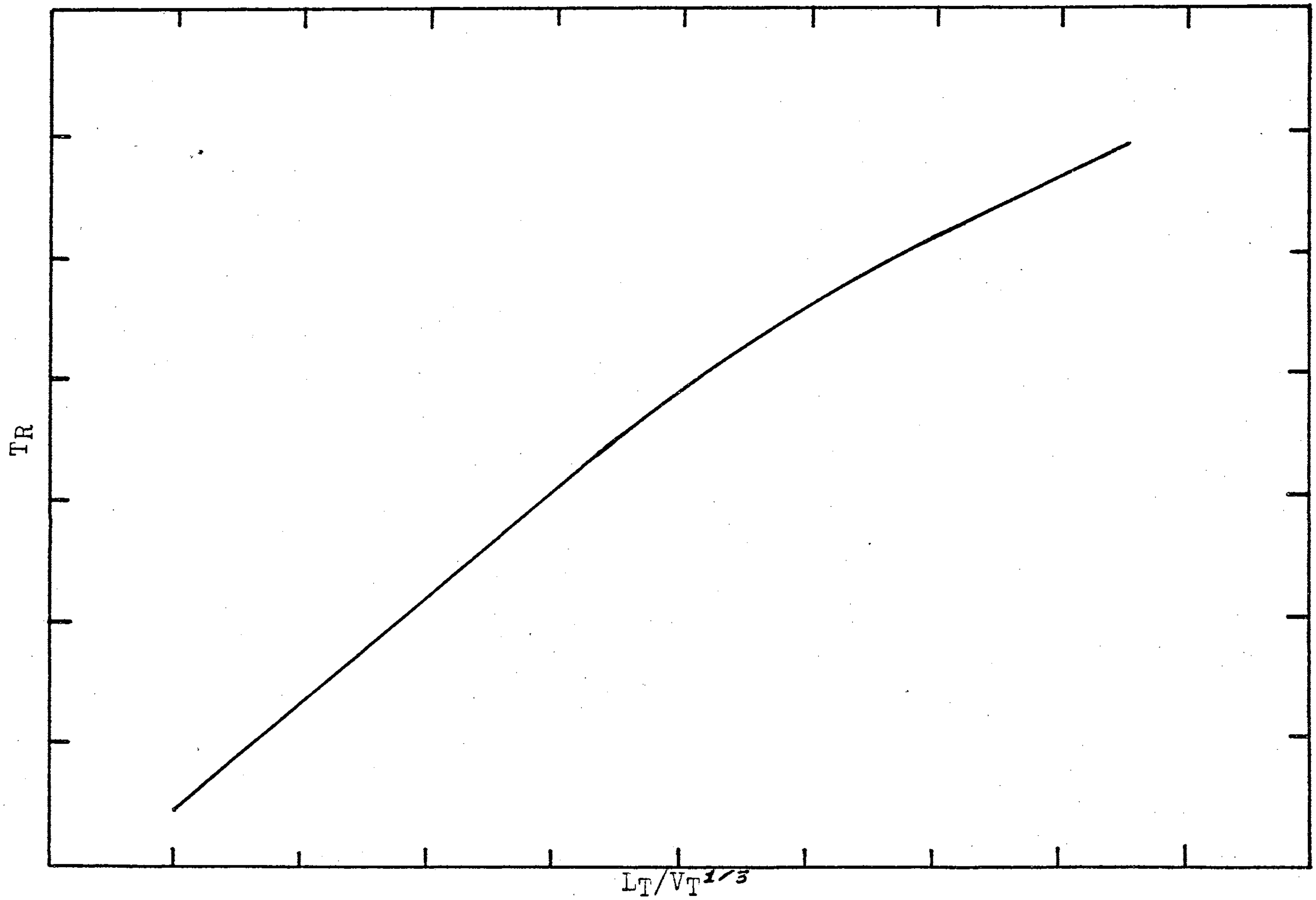

Figure 16. Reduced Temperature vs a Function of the Intermolecular Free Length

Appendix C gives a few of the results of this procedure applied to both non-associated and associated liquids. When used on associated liquids (polymeric species), the resultant L is that L which would obtain in a non-associated liquid (monomeric species) of the same density. This is related to the fact that the thermal expansion of a liquid is an intermolecular phenomenon and is not dependent (for small temperature intervals) upon the size of the molecular species involved. Also implicit in this technique is the assumption that the degree of association does not vary significantly over modest temperature ranges (10 to 20°C).

To determine L_{poly} it is necessary to use either equation (1) or equation (5), i. e., empirical expressions. These expressions give the actual mean intermolecular free length between the surfaces of the polymeric clusters. Figure 1 depicts the difference between these two cases. Also equation (6) may be used to determine L_{poly}. The expression is obtained from equations (1) and (2) as follows. Substitute β_{ad} from equation (1) into equation (2), giving

$$\frac{1}{u^2 \rho} = k' \cdot L^P$$

Taking the square root of both sides results in

$$\frac{1}{u \rho^{1/2}} = k \cdot L^{P/2}$$

Rearranging and letting $p = 2.00$ gives equation (6)

$$u\rho^{1/2}L = K(T) \tag{6}$$

where $K(T) = 1/k = 1/\sqrt{k'}$.

With L_{mono} and L_{poly} having been determined, relation (12) is used to calculate X. This value of X is used to modify the molecular weight of the species in an associated liquid.

APPENDIX B

It is the purpose of the following discussion to analyze in some detail the nature of the transmission of plane waves in matter. The derivation is essentially that of Blitz (2).

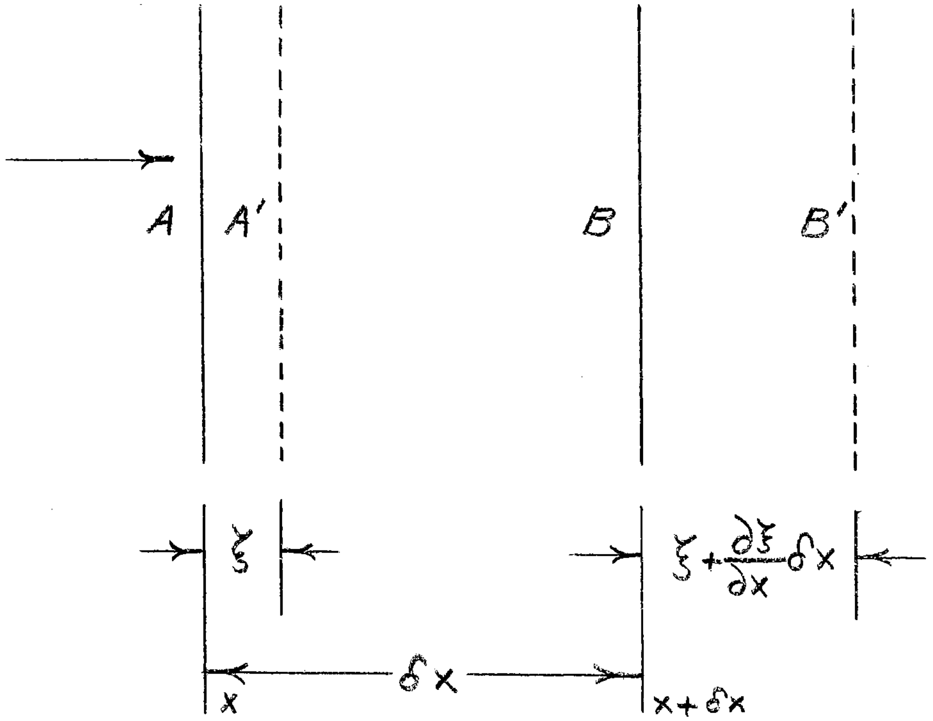

Figure 2.3. (2) Strain on a Layer of Homogeneous Material due to the Passage Through It of Longitudinal Plane Waves.

Figure 2.3 (2) is an idealized schematic of the resultant strain suffered by the transmitting medium caused by the passage of a sonic front (plane wave). From Hooke's Law (small deformation)

$$p = -E \frac{\partial \xi}{\partial x} \tag{20}$$

where $-\frac{\partial \xi}{\partial x}$ is the strain. In the general case the variations in the strain occur so rapidly that thermal relaxation never has an opportunity to set in. Thus, the adiabatic value of the modulus of elasticity E is used.

In terms of the condensation s equation (20) can be written

$$p = E s \tag{21}$$

Now, let the acoustic pressure at A be p and that at B $p + \left(\frac{\partial p}{\partial x}\right) \delta x$, so that the net acoustic pressure acting upon the element AB is $-\left(\frac{\partial p}{\partial x}\right) \delta x$. According to Newton's second law

$$-\left(\frac{\partial p}{\partial x}\right) \delta x = \rho \delta x \frac{\partial^2 \xi}{\partial t^2}$$

or

$$\frac{\partial p}{\partial x} = -\rho \frac{\partial^2 \xi}{\partial t^2} \tag{22}$$

The equation of motion of a plane wave is (2)

$$\frac{\partial^2 \xi}{\partial t^2} = u^2 \frac{\partial^2 \xi}{\partial x^2} \tag{23}$$

and from this and (22) is obtained

~~$u^2 = \frac{E}{\rho}$ (24)~~

For a liquid the modulus of elasticity E can be replaced by $1/\beta_{ad}$. This gives the familiar equation

$$u^2 = \frac{1}{\beta_{ad}\rho} \tag{1}$$

APPENDIX C

In this section a number of the calculational procecures alluded to in the text are discussed in more detail.

If the density of a liquid is known at two temperatures, equation (10) permits an evaluation of the critical temperature, T_c. (In the case of an associated liquid the apparent critical temperature, $T_{c\ app}$, is obtained, because the degree of association decreases with increasing temperature. This results in a calculated $T_{c\ app}$ which is higher than the actual critical temperature, T_c.)

$$\frac{\rho_{T_1}}{\rho_{T_2}} = \frac{\left[1 + \left(\frac{C}{2}\right) - \left(\frac{C}{2}\right)\left(1 - T_{R2}\right)^{P}\right]^{3}}{\left[1 + \left(\frac{C}{2}\right) - \left(\frac{C}{2}\right)\left(1 - T_{R1}\right)^{P}\right]^{3}}$$

Since $T_{R1} = T_1/T_c$ and $T_{R2} = T_2/T_c$, the critical temperature T_c can be determined. However, a graphical solution is much simpler, and Figure 15 was constructed for this purpose.

Figure 16 is a plot of equation (11), from which L_T/V_T can be calculated at any temperature. $V_T = M/\rho_T$ can be obtained, leading to L_T. This value of the intermolecular free length is the value existing between monomeric species as discussed earlier.

Equation (6) gives a calculation of L which represents the intermolecular free length between polymeric species in associating systems and between monomeric species in non-associating systems. This is L_p in equation (12), whereas equation (11) gives the L_m.

To account for the variation in the degree of association with temperature for the high association numbers the following procedure was employed. The calculated value of X (equation 12) is assumed to be the correct value at one-half the distance between the two temperatures used in calculating L_m. Once a few such points of X are obtained, a plot of X versus T can be drawn from which other values of X can be calculated. This method results in the arrows of Figure 2, drawn to indicate the temperature correction.

APPENDIX D

Table V illustrates the lack of precision of the present correlation. Column 1 gives the weight percents of the two systems at three different temperatures. These are the same points which are presented in Table IV and in Figure 2. In column 2 are the literature values for the viscosity (here given as fluidity) which were used in developing the correlation. Columns 3 and 4 give the calculated viscosities (here given as fluidities), determined from Reyburn's modified correlation (Figure 2). The percent error, calculated from

$$\%\ \text{error} = \frac{\phi_{\text{experimental}} - \phi_{\text{calculated}}}{\phi_{\text{calculated}}}$$

is given in columns 5 and 6.

The points for which no analysis is given (to the left of line AB in Figure 2) do not satisfy the assumptions of Jacobson's theory, as mentioned in Chapter V. Points plotting close to, but to the left of line AB in Figure 2, were corrected for variation in X as explained in Appendix C and included in this analysis.

An examination of Figure 2 reveals that the abscissa is off by less than 10% in most instances---a situation which could be corrected by analyzing consistent, single-source

TABLE V

ERROR ANALYSIS

Methyl Alcohol-Water

1 Weight % Alcohol	2 Experimental Viscosity $(Cp)^{-1}$ (38)	3 Calculated Viscosity @ 25°C	4 Calculated Viscosity @ 45°C	5 % error at 25°C	6 % error at 45°C
At 20°C					
0	0.9950	--	--	--	--
10	0.7981	--	--	--	--
20	0.6596	--	--	--	--
30	0.5952	--	--	--	--
40	0.5650	0.315	0.240	80	135
50	0.5562	0.275	0.205	102	171
60	0.5949	0.760	0.680	22	12
70	0.6609	1.060	0.965	38	32
80	0.8389	0.940	0.855	11	2
90	1.1442	1.340	1.240	14	8
100	1.6920	1.710	1.620	1	4
			Average % error	38	52
At 30°C					
0	1.2489	--	--	--	--
10	1.0183	--	--	--	--
20	0.8734	--	--	--	--
30	0.7955	--	--	--	--
40	0.7524	0.705	0.615	7	22
50	0.7337	0.770	0.690	5	6
60	0.7880	1.040	0.960	24	18
70	0.8446	1.335	1.240	37	32
80	1.0373	1.510	1.400	31	25
90	1.3774	1.740	1.640	21	16
100	1.9417	2.090	1.970	7	1
			Average % error	19	17
At 40°C					
0	1.5291	--	--	--	--
10	1.2610	--	--	--	--
20	1.1086	--	--	--	--
30	1.0111	--	--	--	--
40	0.9970	0.980	0.895	2	10
50	0.9569	1.030	0.940	8	2
60	1.0030	1.250	1.150	20	13
70	1.0571	1.550	1.450	32	27
80	1.2755	1.680	1.580	24	19
90	1.6129	1.980	1.860	18	13
100	2.2173	2.310	2.190	4	1
			Average % error	15	17

TABLE V (continued)

Ethyl Alcohol-Water

1	2	3	4	5	6
At 20°C					
0	0.9950	--	--	--	--
10	0.6502	--	--	--	--
20	0.4581	--	--	--	--
30	0.3690	0.369	0.300	0	24
40	0.3436	0.360	0.290	4	19
50	0.3484	0.740	0.660	53	47
60	0.3745	0.900	0.810	58	54
70	0.4219	1.200	1.110	65	62
80	0.4980	0.930	0.840	46	41
100	0.8333	1.270	1.170	34	29
			Average % error	37	39
At 30°C					
0	1.2489	--	--	--	--
10	0.8621	--	--	--	--
20	0.8621	--	--	--	--
30	0.5348	0.670	0.595	20	10
40	0.8834	0.690	0.600	28	39
50	0.8658	1.010	0.910	14	5
60	0.8873	1.120	1.030	21	14
70	0.9416	1.040	0.983	9	4
80	1.0331	1.135	1.068	9	3
100	1.4245	1.350	1.260	5	12
			Average % error	15	12
At 40°C					
0	1.5291	--	--	--	--
10	1.0309	--	--	--	--
20	0.8621	--	--	--	--
30	0.7310	0.731	0.660	0	11
40	1.1198	1.000	0.910	12	23
50	1.0953	1.120	1.030	2	6
60	1.1086	1.450	1.350	24	18
70	1.1682	1.510	1.410	23	17
80	1.2674	1.600	1.500	21	16
100	1.6892	1.550	1.450	9	16
			Average % error	13	15

data. Furthermore, as mentioned in the text, these systems present the severest test for the assumptions of this method; and cluster associating systems of a variety of structures should be analyzed to determine its ultimate value.

NOMENCLATURE

In Order of First Appearance

(Dimensions: L=length, M=mass, t=time, T=temperature)

Quantity	Symbol	Dimensions
Absolute viscosity	μ	M/Lt
Molar volume	V	L^3/mole
Avogadro's number	N	molecules/mole
Molecular diameter	d	L
Constants in Gross and Zimmerman correlation	ζ, q	such that q/V has dimensions M/Lt (i. e., viscosity)
Pressure	p	M/Lt^2
Boltzmann's constant	k	ML^2/t^2T molecule
Temperature	T	T
Ultrasonic velocity	u	L/t
Density	ρ	M/L^3
Entropy	S	ML^2/t^2T
Heat capacity at constant volume	C_v	ML^2/t^2T
Universal gas constant	R	ML^2/t^2T mole

(continued)

Molecular weight or average molecular weight of a mixture	M	M/mole
Constant in Frenkel's equation, describing the structural contribution	A	M/Lt
Activation energy in Frenkel's equation	W	ML^2/t^2
Internal pressure	p_i	M/Lt^2
Internal energy	U	ML^2/t^2
Intermolecular potential energy	U_o	ML^2/t^2
Intermolecular distance in potential functions	r	L
Intermolecular force	F	ML/t^2
Dipole moment	$\bar{\mu}$	
Polarizability	α	
Planck's constant	h	ML^2/t
Zero point electron density fluctuation	ν_o	cycles/t
Heat capacity ratio	γ	
Adiabatic compressibility	β_{ad}	Lt^2/M
Ultrasonic wavelength	λ	L
Interger in Bragg relation	n	

(continued)

Wavelength of light in optical devices	Λ	L
Angle of diffraction	θ	
Shearing stress	τ	M/Lt^2
Fraction of area occupied by the i th class of flow units	$\bar{x}_i$	
Time rate of strain	$\dot{S}$	t^{-1}
Relaxation distance	λ	L
Dimensions of flow unit in plane of shear	λ_2, λ_3	L
Activated state molal enthalpy	$\Delta H^{\ddagger}$	ML^2/t^2 mole
Activated state molal entropy	$\Delta S^{\ddagger}$	ML^2/t^2T mole
Number of significantly different flow units	$\bar{n}$	
Kinematic viscosity	ν	L^2/t
Mole fraction of i th molecular species	x_i	
Constant in viscometer calibration	c_1	
Generalized physical property depending upon the intermolecular free length; e.g., μ, β_{ad} or σ (Surface tension)	j	
Constant in Jacobson's general equation	k_j, p_j	
Intermolecular free length between molecular surfaces	L	L

(continued)

Molecular surface area	Y	L^2
Form factor: actual surface area of molecule divided by spherical surface area inclosing the same volume	f	
Constants in Jacobson's fluidity correlation	k'_j, p'_j	
Free fluidity length		L
Fluidity	ϕ	Lt/M
Constant weakly dependent on temperature	$K(T)$	
Weight fraction of i th molecular species	w_i	
Constants in Jacobson's expanded fluidity correlation	c_j, k''_j	
Constants in Reyburn's correlation	k_n, c_n	
Degree of association	X	
Constants in corresponding states derivation	c, p	
Rao's constant	$\overline{R}$	
Radius of molecular species	r_o	L
Bulk modulus	E	M/Lt^2
Particle displacement	ζ	L

SUBSCRIPTS

Symbol	Meaning
liq	liquid
fr	free
S	"solid-like" molecules
g	"gas-like" molecules
T	at T °K
O	at O °K
a	available
poly=p	polymeric
mono=m	monomeric
c	critical
R	reduced

VITA

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