IN THE NAME OF ALLAH

THE BENEFICIENT

THE MERCIFUL

VISCOSITY MEASUREMENTS OF ACIDIC AQUeOUS SOLUTIONS AS A FUNCTION OF TEMPERATURE

A Dissertation submitted to the
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by

Zulfiqar Ali

DEPARTMENT OF CHEMISTRY
QUAID-I-AZAM UNIVERSITY
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DEDICATED TO MY PARENTS

AND BROTHERS

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ABSTRACT

Relative viscosities for formic, acetic, propionic and butyric acids in aqueous solutions were determined using a thermostated Ubbelohde flow viscometer in the temperature of 25°C to 65°C. From the experimental results, excess viscosities η^{E}, excess volumes ΔV^{E} and flow activation energies E_{η} were calculated using Arrhenius type and Eyring type equations. Free energy of activation $\Delta G^{\ddagger}$, activation entropy $\Delta S^{\ddagger}$ and activation enthalpies $\Delta H^{\ddagger}$ were also evaluated. Explanations of these quantities in terms of acid-acid, acid-water and water-water interactions have been given with special emphasis on hydrogen bonding in solutions.

This is to certify that this dissertation submitted by Mr. Zulfiqar Ali, is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad as satisfying the dissertation requirements for the degree of MASTER OF PHILOSOPHY in Physical Chemistry.

Supervisor: Dr. Mohammad Afzal

External Examiner: ____________________

Chairman: Dr. Afzal Ahmad

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CHAPTER - 1

INTRODUCTION

Viscosity is a property which opposes the relative motion of the immediately adjacent fluid layers. This frictional resistance is due to the transfer of translational energy of momentum[1] from the more rapidly moving layer to the more slowely moving one when the fluid is exposed to the shearing force. In a gas the momentum is transferred by the actual flight of molecules between the layers and the intermolecular collisions at the ends of the free paths of these flights. In a liquid by contrast the momentum transfer is due to intermolecular[2] attractive forces between the molecules, which cause a fractional drag between the moving layers. The flow of a fluid is said to be laminar[3] if points fixed in the fluid move smoothly in layers, one layer (lamina) sliding relative to another. The elementary process involved in laminar flow is pictured in fig. (1), which represent a small region of the fluid. The x-axis is chosen to lie in the local direction of flow, the z-axis perpendicular to the laminae; V_x represent the velocityof fluid in the x-direction. Viscous effect come into play if an element of the fluid is caused to change its shape as it moves. The coefficient of viscosity η (expressed in poise) is defined as the force per unit area needed to maintain the unit difference of velocity between parallel layers in the fluid one centimeter apart

$$f_x = \eta \frac{\partial V_x}{\partial z} \qquad \ldots\ldots (1)$$

where f_x is the shearing force per unit area exerted in the direction of flow on the element of fluid between two

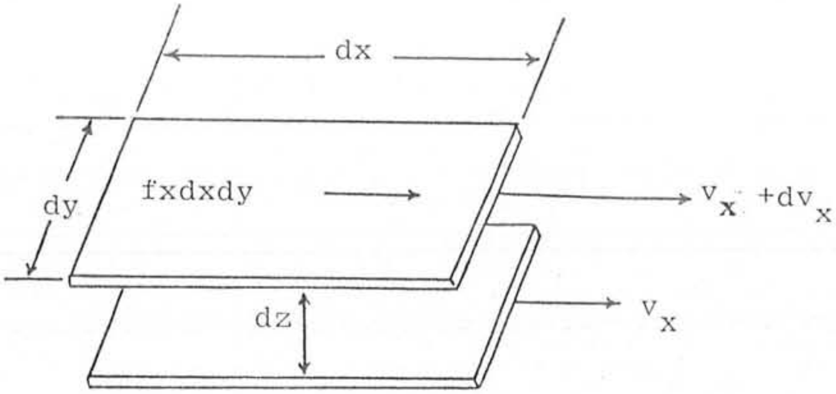


Figure-1. The quantities involved in equation (1) defining the coefficient of viscosity. Acting on the plane of area dxdy is the shearing force fxdxdy, which maintain the velocity gradient dV_x/dz. The shearing force per unit area fx is proportional to dV_x/dz.

planes at the plane of larger z (an equal and opposit shearing force acts on the opposite face) and $\frac{\partial V_x}{\partial z}$ is the velocity gradient in the z direction. The coefficient η depends on temperature, pressure, and composition. A fluid is said to be newtonian fluid if, in laminar flow, η is constant independent of the velociy gradient. The cgs unit for viscosity (grams per centimeter per second) is called the poise.

The hydrodynamic[4-6] theories for liquid and gas flow are very similar. The kinetic molecular mechanisms differ as we might suspect from the different ways in which gas and liquid viscosities depend on temperature and pressure[7-8]. On the basis of the different temperature dependence of the viscocities of a liquids and gases, one must conclude that the mechanism of flow is different for gases than for liquid. For a gas, viscosity increases with temperature and is practically independent of pressure[2]. For a liquid viscosity increases with pressure and decreases with increasing temperature. The kinetic theory of gases ascribes viscosity to a transfer of momentum from one moving layer to another. As a result of the thermal motion, molecules may cross from one layer to another. The friçtion force between two layers of different velocities results from the fact that molecules crossing from the faster to the slower layer transport more momentum, on the average, than the molecules passing in the reverse direction. Momentum is flowing, therefore, from the faster to the slower layers. This transport of momentum tends to counteract the velocity gradient set up by the shearing forces acting in the gases.

The viscous[9] behaviour of gases is fairly well understood according to the kinetic theory of gases, that of liquid is still only partially understood. For one thing the density of the molecules per unit volume in the liquid is so many times higher than in gases that transfer of momentum by the simple occasional collisions of single molecule does not form a good approximation.

Because there are no strong binding forces between them, as is the case with solids, the layers of molecules in the slowly slide over one another under the influence of outside pressure. The viscosity of a liquid is a measure of the frictional force between the parallel layers in motion, which arises from the attractive force between neighbouring layers of groups of molecules, and therefore the measure of viscosity of different mixtures and at various temperatures[7,10] can give information about the behaviour of these forces.

The typical dependence of liquid viscosity on temperature was first pointed out by J. deGuzmann Carrancio in 1913. The viscosity coefficient may be written

$$\eta = A \exp \left(\frac{\Delta Evis}{RT}\right)$$

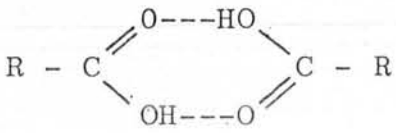
The quantity ΔEvis is the energy barrier that must be overcome[11] before the elementary process can occur. It is expressed per mole of liquid. The term ($-\Delta$Evis/RT) can then be explained as a Boltzman factor giving the fraction of the molecules having the requiste energy to surmount the barrier. Thus, ΔEvis is an activation[12] energy for viscous flow. When the viscosity of a liquid over a range of temperature is plotted as $\ln\eta$ vs T^{-1} a linear graph is usually obtained[7].

Present investigation[13] were done to study the nature of association of simple bifunctional organic molecules in aqueous solution. We are reporting here viscosity results for carboxylic acid[14-17] (i.e. formic, acetic, propionic and butyric acid) in aqueous solutions. The particular aspect under which the association[18] of these molecules is of interest is the hydrophobic interaction. The contribution of hydrophobic bonds[19] to the stability of protein conformation in aqueous solution has been considered by several investigators. Nemethy and Scheraga[20] developed a theoretical treatment of these interactions which predicts among other thing, the thermodynamic parameters for pairwise hydrophobic bond formation between non-polar side chain. In order to verify and extent conclusions of this theory, experimental results are required on an adequate model system. Dimers of small hydrocarbon molecules in aqueous solution would be the most satisfactory model, but such dimers will not form because of the low solubility of hydrocarbon in aqueous solution. This necessitates the use of model compounds containing polar groups.

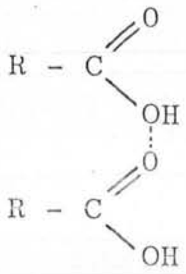
The carboxylic acids represent a useful series of such model compounds. It has been shown by several groups of investigators[21-25] that the carboxylic acids[26-32] dimerize in aqueous solution. Rossotti and Coworkers[33] have carried out the most extensive series of measurements and have shown that, while higher oligomers form in the solution of the acids after acetic, dimerization is the major process occuring over most of the low concentration range for all the acids investigated. The work of Rossotti, el al[24-25] has been attacked by Danielsson and Suominen[34], who showed that changes in the nature of the ionic medium in which the potentiometric titrations were carried out led to the most of the deviation in the titration curves which Rossotti el al had interpreted as being due to polynuclear complex formation.

There has been some contraversy regarding the reality of acid-acid association[34-35]. The argument was that medium effect might have been overlooked. This difficulty arose because it was not clear whether the observed effect is to be counted as a structural effect or as a background effect.

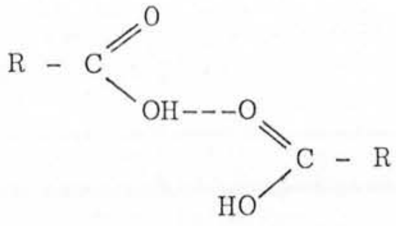
For various qualitative reasons the dimers were expected to be of one of the extended forms (II) or (III) not of the cyclic form[36].



(I)



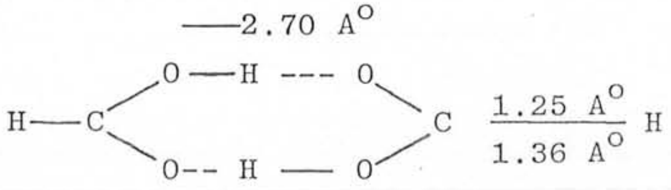
(II)



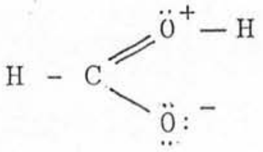
(III)

The dimerization constants increase as a function of the chain length of the carboxylic acid. Such a chain length dependence does not appear in the dimerization constants measured in nonaqueous solvents[37] where the dimers are assumed to be primarly cyclic i.e. of the (I) form.

The hydrogen bonds formed by water are not sufficiently strong to lead to an appreciable concentration of polymerized molecules in the vapour phase. The oxygen atoms of carboxyl group can, however form stronger hydrogen bonds leading to the formation of stable double molecules of formic acid. The structure of the formic acid dimer as determined by the electron diffraction method$^{37-38}$ is the following



The value 2.70 A^{o} for the O — H --- O distance in this substance is smaller than that in ice, 2.76 A^{o}, as expected for this stronger bond. The distance from each hydrogen atom to the nearer of the two adjacent oxygen atoms in the dimers of acetic acid has been reported^{39} to be 1.075 ± .0.15 A^{o}, this is considerably greater than the value 1.01 A^{o} for ice, as is to be expected in consequence of the increased strength of the hydrogen bond can be accounted for in the following way. The resonance of the molecule to the structure



gives a resultant positive charge to the oxygen atom which donates the proton in hydrogen bond formation and thus increase the ionic character of the O - H bond and the positive charge of the hydrogen atom. It also give to the other oxygen atom, the proton acceptor, an increased negative charge. Both of these effects operate to increase the strength of the O-H---O bond.

Properties of pure carboxylic acid and the properties of their mixture have been discussed in term of formation of cyclic dimers and of strong attractive interaction[40-41] between the monomer and the cyclic acid dimers. We have also investigated the thermodynamic and transport properties of binary liquid mixtures. The excess viscosity (η^E), excess volume (ΔV^E) Flow energy of activation (E_η) and various thermodynamic parameters of activation of viscous flow have been determined from the experimental results on densities and viscosities for the system of carboxylic acids (i.e. formic, acetic propanoic and butyric acids) in aqueous solution at different temperatures from 25°C to 65°C.

HISTORICAL BACKGROUND

Poiseuille[42] the great pioneer in research on viscosity, found that some salts increase the viscosity of water whereas others decrease the viscosity. Sprung[43] (1876) appears to have been the first to measure solutions of barium chloride and found that it increased the viscosity of water. His viscosity-concentration curves are approximately linear but have an upword trend at higher concentration which indicates an increasing deviation from a linear limiting law. Arrhenius[44] also found that the linear relationship holds approximately over the lower part of the concentration range but that the viscosity increases more rapidly than the concentration at high concentrations. He proposed an equation which is reducible to the form $\eta = A^c$, η is the relative viscosity compared to that of water at the same temperature and A is an empirical constant for any salt and temperature and this equation is only a rough approximation. This equation has been tested by Reyher[45], by Wagner[46] and by others and found to hold within a few tenth of 1 percent.

Sutherland[47] suggests that the depolymerization of triple water molecules by the dissolved salt causes diminution in viscosity.

The next outstanding investigator on this subject was E. Gruneisen[48], who made a careful and critical study of the experimental technique with the Ostwald form of viscometer and then made measurements, which are probably more precise than any previously made, on aqueous solution of sixteen salts and of sucrose over a wide range of concentrations.

Einstein[49] in 1906 deduced from the principles of hydrodynamics that if the solute could be regarded as made up of spherical incompressible uncharged particles which are large in comparison with the molecules of the water the viscosity of the solution would be $\eta = 1 + 2.5\theta$, where θ is the total volume of the solute particles per unit volume of solution.

Appleby, Schneider and Merton[50], found the Gruneisen effect with other salts, but they did not give a satisfactory interpretation or derived a valid equation for the variation of the viscosity with the concentration.

The work of Merton[51] on cesium nitrate appears to be the most accurate and extensive study of salt which diminishes the viscosity of water. His work confirms the observation of applebey on lithium nitrate that at low temperature, negative slopes and negative curvatures are more pronounced than at high temperature.

The various hypotheses which have been suggested to account for negative viscosity are discussed at considerable length by Robinovich[52]. He concluded that depolymerization of water molecules must be responsible for negative viscosity.

Finkelstein[53] extended Einstein treatment to solution of binary electrolytes in polar solvents. He investigated mathematically the effect on the viscosity of the relaxation time of the solvent dipoles and concluded that the electric influence of the ions on the polar solvent will increase the viscosity proportionality to the concentration. Neither Einstein nor Finkelstein account for the fact that some solute diminish the viscosity of wat

Schneider[54] has made measurements similar to Gruneisens with many other salts, although with less precision, and obtained similar results, showing that Gruneisen's observation of negative curvature of the viscosity - concentration curves at low concentrations is a general one. He made no advance in the interpretation of the phenomena.

Jones and Dole[55] also measured the viscosity of Barium chloride. It predicted that at very low concentrations the viscosity of solutions of all strong electrolytes will be greater than that of water, including salts which at moderate concentrations show diminished viscosity.

Cohen and Turnbell[56] derived from fundamental consideration a relationship between temperature and free volume which seems to unify the original Doolittle free volume equation.

The thermodynamic dissociation constants (Ka) of many carboxylic acids in aqueous solution have been obtained by conductivity measurements. Where a considerable concentration range has been covered, Ka decreases with the concentration, and

Katchalsky Eisenberg, and Lifson[21] considered this can be attributed to dimerization. Their value for dimer dissociation constant Kd, where Kd = HA / H_2A_2 , is 6.2 for acetic acid, which is in good agreement with 5.4 derived by MacDougall and Blumer[57] from vapour pressure. However as Davis and Griffiths[58] have pointed out, MacDougall and Blumers fingure is based upon erroneous data, and more reasonable estimate gives Kd = 20 ± 3 by this method. Davis and Griffiths themselves from careful analysis of freezing point and distribution measurements, obtained Kd $\sim$ 30. These last two values therefore suggest that the figure of 6.2 from conductivity is too small, and a reason for this may be the neglect of the viscosities of acetic acid solutions, which increase with the acid concentration.

This point has been considered by Davies[58] with reference to the evaluation of the dissociation constant Ka. MacInnes[59] and Shedlovsky conductivity measurements lead to concentration dissociation constants and when the log values of these are plotted against Ci (where Ci is the ionic concentration), the plot should be linear, according to the Deby and Huckels theory Davis showed that if $\Lambda\eta/\eta_o$ is used instead of Λ , where η is the viscosity of solution and η_o is that of water, the plot is linear to much higher concentration.

Several investigators[16,19,24] has shown that the carbo xylic acids dimerize in aqueous solution. Rossotti and Coworkers[60-61] have carried out the most extensive series of measurement

The work of Rossotti has been attacked by Danielsson and Summinen who showed that change in the nature of the ionic medium in which the potentiometric titration were carried out led to most of the deviation in the titration curves which Rossotti had interpreted as being due to polynuclear complex formation.

H.G. Hertz and R. Tutsch[13] also investigated the nature of association of simple bifunctional organic molecules i.e. carboxylic acid in aqueous solution.

P.Huyskens, N. Felex[62] and F. Kapukun have also studied the influence of the dielectric constant on the viscosities and on the formation of conductance ions in binary carboxylic acids.

CHAPTER - 2

THEORETICAL

Flow as a Rate Process.

Since the flow of a liquid is a rate process[63-67], in so far as it takes place with a definite velocity under given conditions, it seems reasonable to suppose that the theory of the absolute reaction rates[68-70] can be applied to the problem of the viscosity. Consider two layers of molecules in a liquid at a distance λ_1 apart, and suppose that one slides past the other under the influence of an applied force; if f is the force per square centimeter tending to displace one layer with respect to the other and Δu is the difference in the velocity of the two layers, then by definition

$$\eta \equiv \frac{f \lambda_1}{\Delta u} \qquad \ldots . (1)$$

Where η is the coefficient of viscosity . The motion of one layer with respect to another is assumed to involve the passage of a molecule from one equilibrium position to another such position in the same layer.[71] In order that this passage shall occur, it is necessary that a suitable hole or site shall be available, and the production of such a site requires the expenditure of energy since work must be done in pushing back other molecules. The jump of the moving molecule from one equilibrium position to the next may thus be regarded as equivalent to the passage of the system over a potential energy barrier[72].

Let λ be the distance between two equilibrium positions in the direction of motion, the distance between neighbouring molecules in the same direction being λ_3. The mean distance between two adjacent molecules in the moving layers at right angles to the direction of motion is λ_2 as shown in figure (1).

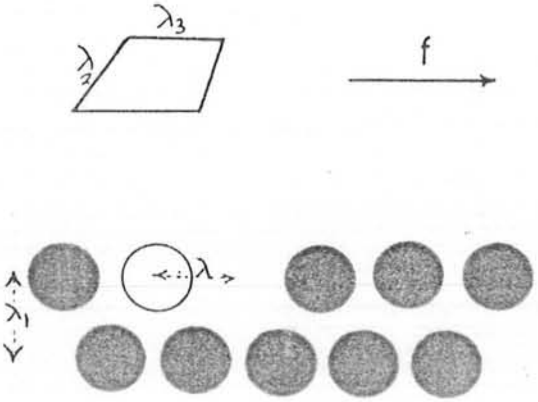


Figure 1. Distance between molecules in a liquid; λ is the distance between two equilibrium position.

It is reasonable to suppose that the potential energy barrier is a symmetrical one, and so the distance between the initial equilibrium position and the activated state, i.e., the top of the barrier is $\frac{1}{2}\lambda$, i.e. the half the distance between the initial and final positions of the molecules. The applied force acting on a single molecule in the direction of motion is f λ_2 λ_3, since λ_2 λ_3 is the effective area per molecule; hence the energy that the moving molecule acquires when it has reached the top of the potential energy barrier is $f\lambda_2\lambda_3 \times \frac{1}{2}\lambda$, i.e., $\frac{1}{2}$ f $\lambda_2\lambda_3\lambda$. The effect of the force causing the flow of a liquid is thus to reduce the height of the energy barrier in the forward direction by an amount $\frac{1}{2}f\lambda_2\lambda_3\lambda$, and the height in the opposite direction will be raised by the same amount.

If ϵ_o is the energy of activation at 0,K^o, i.e., the height of the barrier, when no force is acting on liquid then the

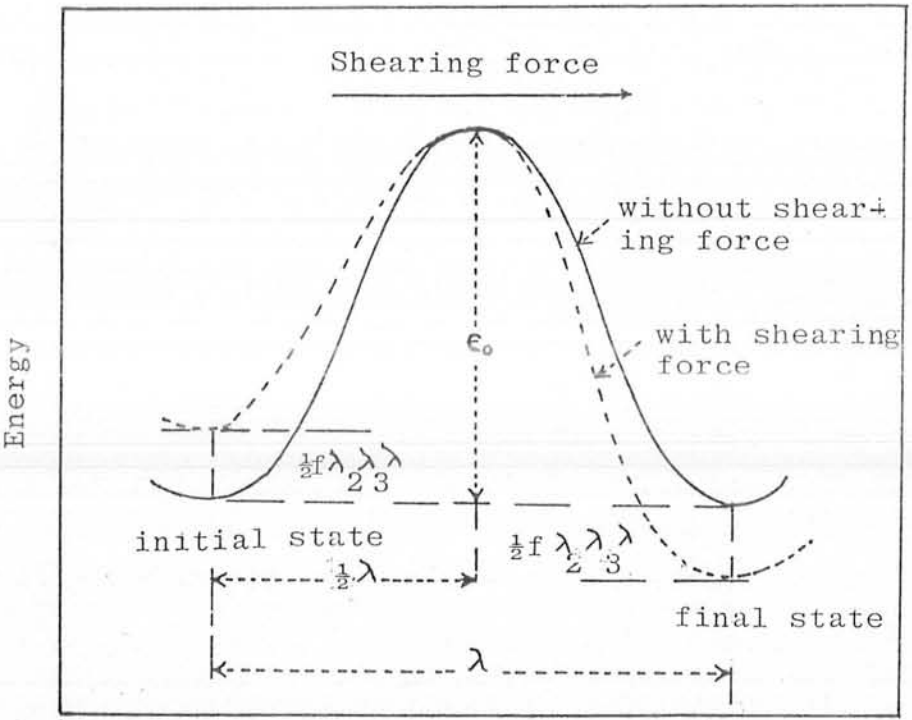


Figure 2. Potential energy barrier for viscous flow, with and and without shearing force.

number of times a molecule passes over the barrier, and hence moves in any direction, per second is given by

$$K = \frac{kT}{h} . \frac{F^{\ddagger}}{F} - e^{-\epsilon_o/kT} \qquad \text{..... (2)}$$

it being assumed that the transmission coefficient K is unity and the tunneling factor being neglected. In this equation $F^{\ddagger}$ and F are the partition functions, for unit volume, of the molecule in the activated and initial states respectively. Since the height of the barrier is altered by $\frac{1}{2}f\lambda_2\lambda_3\lambda$ when the force causing the liquid to flow is applied, the specific rate of flow in the forward direction, i.e. in the direction of force is

$$K_f = \frac{kT}{h}.\frac{F^{\ddagger}}{F}\, e^{-(\epsilon_o-\frac{1}{2}f\lambda_2\lambda_3\lambda)/kT} \qquad \ldots\ldots (3)$$

$$= \frac{kT}{h}.\frac{F^{\ddagger}}{F}\, e^{-\epsilon_o/kT}.\, e^{\frac{1}{2}f\lambda_2\lambda_3\lambda/kT}$$

$$= K e^{\frac{1}{2}f\lambda_2\lambda_3\lambda/kT} \qquad \ldots\ldots (4)$$

and the specific rate in the backward direction will be :

$$K_b = K e^{-\frac{1}{2}f\lambda_2\lambda_3\lambda/kT} \qquad \ldots\ldots (5)$$

Each time a molecule passes over the potential energy barrier, it moves through a distance λ; and since K_f and K_b give the numbers of times a molecule traverses respectively, it follow that the distance moved by the molecule per second, and hence also the rate of motion of the layer, is given by $K_f\lambda$ in one direction and $K_b\lambda$ in the other. The net rate of flow in the forward direction as a result of the application of the force f, which by definition is Δu, is thus equal to $(K_f - K_b)\lambda$;

$$\Delta u = (\kappa_f - \kappa_b) \lambda$$

$$= (\kappa e^{\frac{1}{2} f \lambda_2 \lambda_3 \lambda / kT} - e^{- \frac{1}{2} f \lambda_2 \lambda_3 \lambda}) \lambda \qquad \ldots\ldots (6)$$

$$= 2 \lambda \kappa \, \mathrm{Sinh} \frac{f \lambda_2 \lambda_3 \lambda}{2kT} \qquad \ldots\ldots (7)$$

If the relationship from equation (1) for coefficient of viscosity is introduced, it follows

$$\eta = \frac{\lambda_1 f}{2 \lambda \kappa \, \mathrm{Sinh}(f \lambda_2 \lambda_3 \lambda / 2kT)} \qquad \ldots\ldots (8)$$

For ordinary viscous flow, f is relatively small, of the order of 1 dyne per sq. cm; and since λ_2, λ_3 and λ are all of about molecular dimensions, i.e. 10^{-8} cm; it follows that $2kT \gg f \lambda_2 \lambda_3 \lambda$. It is thus possible, in expending the exponentials included in equation (8), to neglect all terms beyond the first; the result is

$$\eta = \frac{\lambda_1 f . 2kT}{2 \lambda \kappa f \lambda_2 \lambda_3 \lambda} \qquad \ldots\ldots (9)$$

$$= \frac{\lambda_1 kT}{\lambda_2 \lambda_3 \lambda^2 \kappa}$$

If the expression for the frequency κ, as given by (2) is now inserted in (9).

$$= \frac{\lambda_{1} kT}{\lambda_2 \lambda_3 \lambda^2 \frac{kT}{h} \frac{F^{++}}{F} e^{- \epsilon_o / kT}}$$

$$\eta = \frac{\lambda_1 h}{\lambda_2 \lambda_3 \lambda^2} \frac{F}{F^{\ddagger}} e^{\epsilon_o/kT} \qquad \ldots\ldots (10)$$

Although λ is not necessarily equal to λ_1, the two quantities are of the same order of magnitude; and as a first approximation, they are taken to be identical, equation (10) can be written as

$$\eta = \frac{h}{\lambda_2 \lambda_3 \lambda_1} . \frac{F}{F^{\ddagger}} e^{\epsilon_o/kT} \qquad \ldots\ldots (11)$$

The product $\lambda_2 \lambda_3 \lambda_1$ is approximately the volume inhabited by a single molecule in the liquid state, and hence it may be put equal to V/N, where V is the molar volume and N is the Avogadro's number;

$$\eta = \frac{hN}{V} . \frac{F}{F^{\ddagger}} e^{\epsilon_o/kT} \qquad \ldots\ldots (12)$$

This equation may be written in another form

$$K^{\ddagger} = \frac{F^{\ddagger}}{F} e^{-\epsilon_o/kT} \qquad \ldots\ldots (13)$$

and the kinetic relationship

$$K^{\ddagger} = e^{-\Delta F^{\ddagger}/RT} \qquad \ldots\ldots (14)$$

Where $\Delta F^{\ddagger}$ is the standard free energy of activation per mole.. It follows from equation (12).

$$\eta = \frac{hN}{V} e^{\Delta F^{\ddagger}/RT} \quad \text{..... (15)}$$

Further, since $\Delta F^{\ddagger}$ may be replaced by $\Delta H^{\ddagger} - T\Delta S^{\ddagger}$

$$\eta = (\frac{hN}{V} e^{-\Delta S^{\ddagger}/R}) e^{\Delta H^{\ddagger}/RT} \quad \text{..... (16)}$$

Since the molar volume of a liquid does not vary greatly with the temperature and $\Delta S^{\ddagger}$ being taken constant, equation (16) takes the form

$$\eta = Be^{E_{vis}/RT} \quad \text{..... (17)}$$

A relationship of this kind was suggested empirically by S. Arrhenius[73] and by J. de Guzman[74] and derived theoretically in a manner different from that given above by E.N. da C.Andrade[75]. The partition function for a molecule of liquid may be written

$$F = \frac{(2\pi mkT)^{3/2}}{h^3} V_f bl\ e^{-E_o/RT} \quad \text{..... (18)}$$

where the first term on the right hand side is the translational contribution of a single molecule moving in its free volume V_f; bl is the combined rotational and vibrational partition function. The chief difference between a molecule in the initial state and one in the activated state for flow is that the latter has one degree of translational freedom less than the former and if the product of F_{rot} and F_{vib} is almost the same in the two states, as it generally will be since the corresponding degrees of freedom are not affected.

$$\frac{F}{F\ddagger} = \frac{(2\pi m\ kT)^{\frac{1}{2}}}{h} V_f^{1/3} \qquad \ldots\ldots (19)$$

substituting this term in equation (12) gives

$$\eta = \frac{N}{V} (2\pi m\ kT)^{\frac{1}{2}} V_f^{1/3} e^{\epsilon_o/kT} \qquad \ldots\ldots (20)$$

The free volume[76] may be represented as,

$$V_f^{1/3} = \frac{cRTV^{1/3}}{N^{1/3}\Delta E_{vap}} \qquad \ldots\ldots (21)$$

Where ΔE_{vap} is the molar energy of vaporization, c is the packing number and V and N molar volume and the Avogadro's number It follows that equation (20) may be written.

$$\eta = \left(\frac{N}{V}\right)^{2/3} \frac{cRT}{\Delta E_{vap}} (2\pi m\ kT)^{\frac{1}{2}} e^{\epsilon_o/kT} \qquad \ldots\ldots (22)$$

Upon taking c as equal to 2, i.e., for cubic packing, inserting the known values for N and k and expressing R in calories, so that ΔE_{vap} is also in calories, equation (22) becomes.

$$\eta = 1.09 \times 10^{-3} \times \frac{M^{\frac{1}{2}}T^{3/2}}{V^{2/3}\Delta E_{vap}} e^{E/RT} \qquad \ldots\ldots (23)$$

Where M is the molecular weight of the substance under consideration and E is the activation energy per mole for viscous flow. According to E.N. daC. Andrade[75] the viscosity of many liquids can be expressed by means of an equation of the form

$$\eta = aV^{1/3}e^{b/T}$$

THEORY OF MIXTURE VISCOSITY[77]

There are two major semiempirical theories of liquid viscosity. The first is the absolute rate theory of Eyring and Coworkers[78]. This relates the viscosity to the free energy needed for a molecule to overcome the attractive force field of its neighbours, so it can jump (flow) to a new equilibrium position. Thus the deviation of mixture viscosity from this equation (24)[79-80].

$$\ln\eta = X_1 \ln\eta_1 + X_2 \ln\eta_2 \qquad \ldots\ldots \quad (24)$$

should be related to free energy more precisely, the excess free energy of mixing[81-82]. The second semiempirical theory is the free volume theory[83-86], which relates the viscosity to the probability of occurance of an empty neighbouring site into which a molecule can jump, so deviation from equation (24) can be attributed to variation in the free volume of the solution.

Combining the absolute rate and free volume theories of viscosity, we can obtain[78,88,87] the viscosity of the solution.

$$\eta = A \exp\left[\Delta G^{\ddagger}/RT + \gamma V^{*}/V_f\right] \qquad \ldots\ldots \quad (25)$$

$\Delta G^{\ddagger}$ is the activation free energy per mole of solution, R is the gas constant and T is the absolute temperature. V^{*} is the empty volume which must be available for a molecular segment jump-ing to its new site, V_f is the volume per segment in the solution, and γ is a factor of order unity. V^* is also identified with the hard-core volume of a segment, and it is therefore implicitly assumed in equation (25) that viscous flow occurs by segmental motion rather than by motion of whole molecules. An equation of the same form hold for a pure components.

$$\eta_i = A \exp \Delta G_i^{\ddagger}/RT + \gamma V^*/V_{f_i} \quad (i=1,2) \qquad .....(26)$$

Where the subscript lables the property of a pure component i. (It should be noted that Macedo and Litovitz[87] write $\Delta E^{\ddagger}$ the energy of activation, for $\Delta G^{\ddagger}$ in these equations).

Following Roseveare, et al[81], we now assume

$$\Delta G^{\ddagger} = X_1 \Delta G_1^{\ddagger} + X_2 \Delta G_2^{\ddagger} - \alpha \Delta G^R \qquad ....(27)$$

Where ΔG^R, the residual free energy[88], is closely related to the excess free energy of mixing[89] α is a constant of order unity. Here α and γ both are equal to unity.

Substitution of equation (27) in equation (25) taking logarithms of the resulting equation and of equation (26) and a simple manipulation then yield[90].

$$\ln\eta = X_1 \ln\eta_1 + X_2 \ln\eta_2 - \frac{\Delta G^R}{RT} + V^*\left(\frac{1}{V_f} - \frac{X_1}{V_{f_1}} - \frac{X_2}{V_{f_2}}\right) \qquad ....(28)$$

The residual free energy of mixing can, in turn, be broken down into enthalpy and entropy contributions.

$$\Delta G^R = \Delta H_M - T\Delta S^R \quad \text{.... (29)}$$

H_M = is the enthalpy of mixing per mole of solution

S^R = is the residual entropy per mole[88], that is the entropy of mixing minus the combinatorial entropy.

The residual entropy differs from the conventionally defined excess entropy of mixing in that the combinatorial entropy is not necessarily computed according to the ideal mixing law for molecules of the same size.

The free volume per segment is defined as the difference between the total volume per segment and the hard-core volume.

$$V_f = V - V^* \quad \text{..... (30)}$$

We define a reduce volume

$$\bar{V} = V/V^* \quad \text{..... (31)}$$

Upon substitution of equation (29-31) in to equation (28) we obtain.

$$= \ln \eta_{id} + \ln \eta_H \ln \eta_S + \ln \eta_V \quad \text{..... (32)}$$

Energy of Activation for Flow and Energy of Vaporization[7].

The energy of activation for viscous flow is related to the work required to from hole in the liquid, the experimentall observed activation energy E_{vis} may be expected to be some fraction of ΔE_{vap}. (The activation energy for viscosity, i.e., ΔE_{vis}, differs from the free energy of activation, $\Delta F^{\ddagger}$). Thus

$$E_{vis} = \frac{\Delta E_{vap}}{n} \qquad \ldots\ldots (33)$$

If the value of E_{vis}, given by equation (33) is now inserted in (23) the result is

$$\eta = 1.09 \times 10^{-3} \times \frac{M^{\frac{1}{2}}T^{3/2}}{V^{2/3}\,\Delta E_{vap}}\, e^{\Delta E_{vap}/nRT} \qquad \ldots\ldots (34)$$

In order to determine the factor n, which gives an indication of the size of the hole necessary for viscous flow, the viscosities were computed from equation (34) by use of integral and half integral values of n from 2 to 5, and the resulting figures for $\log\eta$ plotted against 1/T. For any value of n the plot was either a straight line or, in some cases, a curve slightly convex toward the 1/T axis; the value of n that gave a plot parallel to the straight line of the computed data for $\log\eta$ against 1/T was taken as the correct one. From an examination of the result for a number of substances, it is clear that for most nonassociated liquids, apart from metals, n lies between 3 and 4. It appears that for non polar molecules which have spherical or approximately spherical symmetry n is near 3; but for polar molecules and others, e.g., long-chain hydrocarbons[114] not having spherical symmetry, n is about 4. It is doubtful, however, if a sharp distinction can be drawn, since the value of n increases with the temperature.

$$E_{vis} = R \frac{d \ln \eta}{d(1/T)} \qquad \ldots\ldots (35)$$

E_{vis} can be determined from the plot of log η against 1/T, i.e., in a manner similar to that employed for obtaining the experimental energy of activation energy for chemical reaction. The values E_{vis} as found by this procedure are almost constant for normal liquids, over a range of temperature under ordinary conditions. The energy of vaporization varies only slowly with temperature, and so the ratio $\Delta E_{vap}/E_{vis}$ should be approximately equal to 3 or 4 in the temperature range for which E_{vis} is constant.

Associated Liquids.

The behaviour of associated liquids[7,63] as hydroxylic compounds, is abnormal in several respects, the viscosities are very much higher than for analogous nonassociated substances and the values decreases rapidly with increasing temperature. For instance H_2O is more viscous than H_2S or CH_4; C_2H_5OH and $C_2H_5NH_2$ are much more viscous than propane; aniline and phenol are much more viscous than toluene. This abnormally larg viscosity is, of course due to hydrogen bond structure of these liquids. When a molecule in such a liquid flows it must not only break Wander Waals and dipole "bonds" but also hydrogen bonds. The energy of activation for viscous flow is not independent of temperature[108]. As the temperature is raised, there is a decrease in the number of hydrogen bonds that have been to be brocken before flow can occur, and hence the activation energy decreases; the value observed for water at 150°C[78] is probably free from any appreciable contribution due to structural changes. The high activation energy for the flow of water and other associated liquids accounts for the high viscosities of these substances. When the compound contain two or more hydroxyl groups, as in the glycerol and glycol, for example the viscosity is very high on account of the relatively large number of hydrogen bonds which must be brokwn in the formation of activated for flow.

Entropy of Activation for Flow.

In view of the high activation energy for flow of associated liquids it is a striking fact that the free energy of activation shows no such abnormality. The explanation is that $\Delta F^{\ddagger}$ is equivalent to $\Delta H^{\ddagger} - T\Delta S^{\ddagger}$ and that the high value of the heat of activation $\Delta H^{\ddagger}$ is compensated by the large positive value of $\Delta S^{\ddagger}$, so that $\Delta F^{\ddagger}$ remain normal. If the unit of flow even in associated liquids is a single molecule and the formation of activated state involves the breaking of a number of hydrogen bonds, it is evident that the entropy of the activated state will be appreciably greater than that of the initial state. In other words, the entropy of activation for flow $\Delta S^{\ddagger}$ should be relatively large and positive, in agreement with the experimental fact that $\Delta F^{\ddagger}$ is normal in spite of the high value of $\Delta H^{\ddagger}$ for associated liquids.

It has been seen that for molecules of spherical, or approximately sperical, symmetry, $\Delta E_{vap}/E_{vis}$ is about 3, compared with a value of 4 for non spherical substances; this mean that the energies of activation for flow are relatively larg for the former, and hence, in accordance with the conclusions just reached for associated liquids, the entropy of activation for flow should be comparatively high. The symmetrical molecules are well packed in the normal liquid state. Among the molecules for which n is 3, mention may be made of nitrogen, oxygen, carbon monoxide and argon, which probably have a closed-packed spherical structure in the liquid, and of benzene, naphthalene and cyclohexane.

DENSITY

Density measurements[91-92] afford a most convenient means of aiding the identification, analysis, and characterization of organic substances in either the liquid, solid or gaseous state.

The density measurement furnishes interesting and useful information on molecular forces and structure and its reciprocal defines the specific or molar volume[93-94].

Rules for influence of molecular composition on liquid densities.

(1) In general, density increases with increasing molecular weight.

(2) Polar molecules have greater densities than non-polar molecules of similar molecular weight.

(3) Position isomers and cis-trans isomers are often distinguished by density measurements.

(4) The branching of a carbon chain usually produces relatively small change in density.

(5) The densities of ortho-, meta-, and para-substituted benzenes are nearly always very close together.

(6) The greater the number of heavy (e.g. halogen) or strongly polar (e.g. hydroxyl, nitro) groups per carbon atom in the molecule, the greater is the density.

(7) Polysubstitution on a single carbon leads to higher densities than the same amount of substitution spread along a carbon chain.

DEFINITION AND UNITS :

Density, d, is defined by the equation

$$\begin{aligned} d &= \text{mass/volume} \\ &= m/v \end{aligned} \qquad \text{....} \quad (36)$$

In accordance with the c.g.s. system of units, density measurements are expressed in grams of mass per cubic centimeter. However, this absolute density, d^t,[95] measured at t°C, and defined by the equation-

$$d^t = m/V_{cc}. \text{ g. per cc.} \qquad \text{.....} \quad (37a)$$

is seldom used. More commonly, density measurements are expressed in grams of weight per milliliter, which under most conditions is equivalent to grams of mass per milliliter. Thus the relative density at t°C, is defined by the equation.

$$d_4^t = m/V_{ml}, \text{ g. per ml.} \qquad \text{.....} \quad (37b)$$

By definition, one milliliter = 0.001 per liter = 0.001 part of the volume of one kilogram of pure, ordinary water at its temperature of maximum density (3.98°C). Therefore d_4^t called "density relative to water at 4°C" or specific gravity relative to water at 4°C.

Commonly it is assumed that 1 ml. is equal to 1 cc exactly, but subsequent measurements showed that 1 cc. = 0.999973 ml. that is,

$$V_{cc} = 1.000027 \text{ ml.} \qquad \ldots\ldots (38)$$

The difference between g per cc., d^t, and g. per ml., d_4^t is evidently negligible for most purposes. Moreover, the weight W, is connected with mass, m, by the equation W=mg, , where g, the acceleration due to gravity is a constant for a given geographical location. Hence $W_1/W_2 = m_1/m_2$ provided that both weighings are carried out at the same place. Under this condition, that is when both $V_{ml.}$ and m are determined by weighings in the same laboratory, no change in the numerical value of relative density is caused by using grams of weight instead of grams of mass.

Instead of d^t, d_4^t, is used because it can be accurately and conveniently measured by a direct comparison of the weight of the equal volumes of the substances at t°C and of water at 3.98°C., while values of d^t are ultimately based on the less reliable measurements of the dimensions of some substances and on its absolute mass.

One can also use the specific gravity, d_t^t, which is defined as the mass, m, of a substance at t^{o}C. relative to the mass, m_o, of an equal volume of water at t^{o}C., that is d_t^t is a dimensionless number.

$$d_t^t = (m/V)/(m_o/V) \qquad \ldots\ldots (39)$$

Interconversion of densities.

By combining (37b) and (38) with (37a),

$$d^t = 0.999973\ d_4^t \qquad \ldots\ldots (40)$$

From equations (37a), (37b) and (39)

$$d_4^t = d_t^t \cdot d_4^t\ (H_2O)^{96}$$

and

$$d^t = d_t^t \cdot d^t\ (H_2O)$$

VISCOSITY

One of the transport properties is viscosity,[97-98] which is characteristic property of all fluids, liquids as well as gases. The viscosity is a dynamic[99-100] non-equilibrium property of fluids and is defined as the resistance that one part of a fluid offers to the flow of another part of the fluid, it is a measure of the resistance to flow. A force must be applied to a fluid to cause it to flow-pressure difference- and in the absence of such force, flow stops.

Let us consider a fluid flowing in the x-direction with a non uniform linear velocity V; the velocity increase in the y - direction, as is illustrated in figure (3).

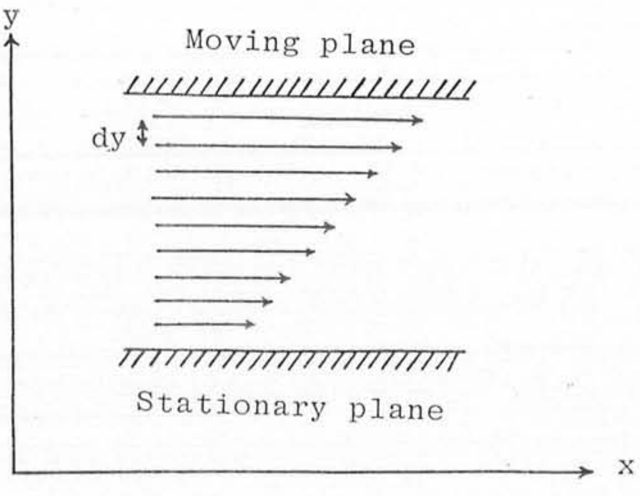


Figure 3.

As a result, the fluid as a whole is broken up into thin layers. Each layer moves with a different velocity. Consider now two layers separated by a distance d_y, as in figure (3). According to our velocity condition, the upper layer (the one close to the moving plane moves faster than the lower one. Consequently, the upper layer is slowed down by the adjacent lower layer, and the lower layer is speeded up by the faster moving upper layer. In order that the two layers keep their velocities unchanged, a force must be applied. The force necessary per unit area, called the shear stress, S, must be proportional to velocity gradient. Thus,

$$S = \frac{f}{A} = \eta \lim_{\Delta y \to 0} \left(\frac{\Delta u}{\Delta y}\right)$$

$$= \eta \frac{du}{dy}$$

Where $\frac{du}{dy}$ is the velocity gradient and η is the viscosity coefficient.[101] As obvious, S has the dimension of pressure. The difference between pressure and stress is that the former is the force per unit area acting perpendicular to the area, where as stress acts parallel to the area. The viscosity coefficient may be thought of as the stress - force per unit area - required to move a layer of fluid with a velocity difference of 1 cm s^{-1} past another parallel layer 1 cm away. The dimensions of in the cgs system are gram per centimeter per second (g $cm^{-1}s^{-1}$). Such a unit is called poise. Since this unit is rather large, viscosities are usually given in contipoise (10^{-2} poise). There are certain other terms which are used particularly with reference to the viscosity of solutions; they are as follows:

1. <u>Absolute Viscosity</u>.

For laminar flow the absolute viscosity can be defined as the force per unit area required to maintain unit difference in velocity between two parallel layers of the fluid which are unit distance apart. It may be written

$$\eta = \frac{\tau}{\partial u/\partial y}$$

$$\tau = \eta \frac{\partial u}{\partial y}$$

2. <u>Kinematic Viscosity (ν)</u>

Kinematic viscosity is defined as the ratio of the absolute viscosity to density

$$\nu = \eta/\rho$$

where ν is the kinematic viscosity. The dimensions in cgs units is cm^2s^{-1}. The unit 1 cm^2s^{-1} is called the stokes but 0.01 stokes or the centistokes is the common practical unit.

3. Relative Viscosity[102] (η_{rel})

The relative viscosity is the ratio of the viscosity of a solution to that of the pure solvent under the same conditions.

$$\eta_{rel} = \eta / \eta^{o}$$

4. Specific Viscosity (η_{sp})

The specific viscosity is the ratio of the difference between the solution and solvent viscosities to the solvent viscosity.

$$\eta_{sp} = \frac{\eta - \eta^{o}}{\eta^{o}}$$

$$= \frac{\eta}{\eta^{o}} - 1$$

$$= \eta_{rel} - 1$$

5. Fluidity (ϕ).

The fluidity, ϕ is defined as the reciprocal of the absolute viscosity.

$$\phi = 1/\eta$$

6. Intrensic Viscosity.

The interinsic viscosity of a solution of concentration c, is given by

$$\lim_{c \to o} \quad (\eta - \eta_o) / (C.\eta_o)$$

or

$$\lim_{C \to o} \quad 1/C \ln (\eta/\eta_o)$$

VISCOSITY OF LIQUIDS

The gas viscosity is said to be due to the momentum transfer by individual collisions between molecules moving randomly between layers with different velocities. A similar momentum transfer may exist in liquids although the molecules in a liquid are much more closely packed than that of the gases. However, they have an average separation between the molecules which allow the collisions and hence momentum transfer. The qualitative concept of liquid viscosity is often expressed by

$$\eta = \eta_m + \eta_i$$

where η_m represents the viscosity contribution as described by a "kinetic theory" picture of momentum transfer and η_i is the contribution of intermolecular forces to the viscosity of liquids.

A review[103] of the theories of liquid viscosity reveals that these theories can be classified somewhat arbitrarily into those based on gas like liquid and those based on solid like liquid. In the former, the liquid is considered to be ordered in a short-range sense but disordered in a long-range view. Distribution functions are calculated from such models and expressions for viscosity obtained.

In the latter type of theory, the liquid is assumed to exist as a regular lattice, momentum transfer resulting from molecules which are assumed to be vibrating within the lattice structure, or moving into nearby holes, or combination of these two events.

The Variation of Viscosity with Temperature.

It has been shown that the temperature dependence[65,104,1] of viscosity is quite different for liquids and gases. The viscosit of liquids decreases with increasing temperature according to the simple expression derived by Andrade[75], (1934).

$$\eta = Ae^{E/RT}$$

where E is constant, R is gas constant, and A is constant. The same type of equation derived by Eyring[63], using a reaction rate theory in which E has been assumed to be an activation energy for shear flow. The rate of flow depends on the net rate at which the molecules pass over an energy barrier, characterized by the activation energy[106].

The kinetic theory of gases ascribes viscosity to a transfer of momentum from one moving layer to another. As a result of the thermal motion, molecules may cross from one layer to another. The friction force between two layers of different velocities result from the fact that molecules crossing from the faster to the slower layer transport more momentum, on the average, than the molecules passing in the reverse direction. Momentum is flowing, therefore from the faster to the slower layer. This transport of momentum tends to counteract the velocity gradient set up by the shear forces acting in the gas. The quantity E_η/R is usually obtained as the slope of a graph for $\ln\eta$ against $1/T$, because equation (3) gives $\ln\eta = \ln A + E_\eta/RT$.

It has long been observed[104] that temperature dependence of associated liquid[97] did not follow the simple expression derived by Andrade[75]. Tammann and Hess[107] have proposed an emprical expression which fits the observed viscosity data in associated liquids. Their equation is

$$\eta = A \exp B/(T - T_{\alpha})$$

where B and T are constants dependent on the liquid involved. An explanation of the unusual temperature dependence of associated liquids[108] is that the activation energy changes with temperature. This activation energy changes with temperature. This activation energy is assumed to be a function of the average hydrogen bonding in the liquids which will decrease with increasing temperature due to the thermal motion of the molecules if one assumes that

$$E = a/T^2$$

where "a" is the activation energy constant dependent on the liquid and T is the absolute temperature. Then the viscosity expression becomes.

$$\eta = A \exp (a/RT^3)$$

There are large number of other such equations, which has been proposed so far. Those most often quoted are of two types: First type of those in which volume dependence is introduced and represented in the forms such as

$$\eta_v x = A.\ e^{B/v^y.T}$$

where v is molar volume and the values of both x and y range from zero to unity[109] second type corresponds to those which are rather modifications of Andrae[75] equation, and introduced another known constant[76,110,111]. A typical example is the Gififalco form[112]

$$\log \eta = c/T^2 + B/T + A$$

where c is about zero except for polar or associated liquids. A more important equation containing exponential temperature dependence has been proposed by Eyring et al[78] from rate processes theory and is useful in high concentration range Eyring equation is.

$$\eta = A.\ e^{\Delta H/RT}$$

where ΔH is the enthalpy of activation.

These equations were derived for pure non associate liquids. In associated liquids[97] such as water or alcohol or carboxylic acid, viscous flow involves distortion of structure in addition to normal molecular friction. Extra energy is therefore needed to promote flow in structured liquids and it is termed 'structural activation energy'.

The amount of structure[113] in an electrolyte solution where the solvent is an associated liquid will in general depend on both temperature and concentration. Temperature will affect the structure through the amount of thermal movement. Concentration alters structural characteristics by reason of ion-solvent interaction, the extent of alteration will depend on the types of ions present and their average separation.

Effect of High Pressure on Low Temperature Liquid Viscosity.

The viscosity of liquids below normal boiling point is not affected by moderate pressures, however, under very high pressures, large increases have been observed. This reveals that for more complex molecular structures, the effect of pressure is larger[114-116], for example, Bridgeman carried out such experiments upto pressures of about 12,000 atm; the frictional increase in the viscosity of liquid mercury was observed to be 0.32; for isobutyl alcohol 790 and for complicated engenol 10^7. Bridgeman's results indicate that a viscosity - pressure plot is linear to a few thousand atmospheres but at higher pressure the plot would be linear if $\ln\eta$ be ploted against pressure. This semi logrithmic correlation is said to be predicted by the hole theory of liquids.

There seems to be no reliable way to estimate low temperature, high-pressure liquids viscosities. Andrade suggested a relationship[117] involving the ratios of the specific volumes and adiabatic-compressibility factors for the compressed and uncompressed liquids but the relationship is only approximate in the linear portion of the η -p curve and does not even approximate the true situation at high pressures.

Viscosities and Molecular Structure

Much emphasis is placed upon relating viscosities to the molecular structure[115,118-119] and many rules have been formulated to relate structural characteristics to viscosity but up to now no reliable quantitative relationship has come forth. Theoretically increasing the molecular weight, the degree of branching, or the ability of the molecule to associate with its neighbours will increase both the viscosity and sensitivity of the viscosity to the temperature changes. Introduction of double bonds usually result into the reduction of viscosity, since even though the resulting molecule is less flexible, there is also less hindrance from the missing hydrogen atoms.

Andrade's equation, which is the best low temperature two constant liquid viscosity relationship, could not help the evaluation of A or β[120]. For example, Kierstead and Tubervitch[118] studies this problem for pure hydrocarbons but could not develop any useful quantitative basis for predicting either A or β structures alone. Anyhow, they came to the following conclusions.

In homologous series, 1/A appears to be a linear function of the number of carbon atoms, but β increases slowly as the number of carbons in the skeleton increases. A, decreases but β increases with branching, but the effect of branching varies; i.e., each branch appears to have more effect than the preceeding one. Unsaturation increases A, and decrease β for similar compounds; cyclic compounds have larger values of β and A than the corresponding aliphatic compounds.

Two attempts to predict the viscosities are presented here as the best estimations available.

a) Sounder's Method[121].

This method is based on empirical relation

$$\log(\log\eta) = \text{m.p.} - 2.9$$

where m is constant equal to (I/M); I being constant calculated from atomic and structural constant[121], and M is the molecular weight. This method is not very accurate.

b) Thomas Method[122].

This method suggests that the liquid viscosities at temperature below normal boiling point may be calculated by the use of expression.

$$\log \left[8.569 \left(\eta / \rho^{\frac{1}{2}} \right) \right] = \theta \left[\frac{1}{T_r} - 1 \right]$$

Where θ is viscosity constant[123] and T_r is the reduced temperature (T/T_c). The errors in viscosity values calculated by this method are quite variable but generally indicate that aromatics (except benzene), mono-halogenated compounds, unsaturated and high molecular weight n-parafins can be treated with errors usually less than 15 percent. This method should not be used for alcohols, acids, naphthenes, heterocyclics, amines, aldehydes or multihalogenated compounds.

c) Other Methods.

Many other empirical estimation techniques have been suggested at various times. Gambill has suggested a new method[124] based on the molal latent heat of vaporization at normal boiling point. Friend and Hargreaves have tried to relate an additive parameter called the rheochor to the viscosity at T_b[125]. Many other workers have proposed relations involving η, T and one or more of the following, T_b, M, vapour density, surface tension, sonic velocity, vander waals volumes, vapour presssure, etc[119-119,126-129].

An interesting relationship was proposed by Bondi[130] to correlate a dimensionless viscosity with a reduced temperature. The values of A and B of his equation were found to be constant for several homologous series and, in fact, were almost the same for most families. The parameters used to nondimensionalize and T were found to be additive functions of the various characterizing groups comprising the molecule.

CHAPTER - 3

EXPERIMENTAL

Methods of Measurements:

There are many methods for measuring viscosities:

A. Capillary Flow.
B. Rotational Viscometer
C. Oscillation Viscometer
D. Falling Body Types
E. Miscellaneous Methods

Of the numerous methods of measuring viscosity the requirement common to all successful methods is that the measurements be made in a system under the following conditions:

1. The flow is every where parallel to the exis of the tube.
2. The flow is steady, initial disturbances due to acceleration from rest having been damped.
3. There is no slip at the walls of the tube.
4. The fluid is incompressible.
5. The fluid will flow when subject to the smallest shearing force, the viscous resistance being proportional to the velocity gradient.

These conditions of flow are promoted by high viscosity and low velocity gradients. In most system when the fluid velocities become sufficiently high the streamlines lose there ordered pattern and the flow becomes turbulent.

For many instruments, the transition from streamlined to turbulent flow may be predicted through the use of a dimensionless quantity known as the Reynolds number

$$R = V\alpha\rho/\eta$$

where ρ is the fluidity density, and v and a are velocity and length characteristic of the system. In a capillary tube the diameter D and the mean velocity $\bar{v}$ are taken as characteristic, and the expression becomes $R = \bar{v}\,D\rho/\eta$. Thus in capillary flow it has been found that turbulance is not to be expected at Reynolds number less than 2000.[131]

Here one of the capillary method is used to determine the viscosity of acidic aqueous solution (i.e. formic, acetic, propanoic and butyric acid).

Capillary Flow:

Since the poiseuille-Hagenback-cutte equation for laminar flow of a fluid through a capillary may be written as

$$\eta = \frac{\pi r^4 Pt}{8v(l+nr)} - \frac{m \rho v}{8\pi(l+nr)t} \qquad \ldots\ldots (1)$$

where,

r = radius of capillary.

P = Mean effective pressure drop through the capillary.

v = volume of the flow in time t.

l = length of the capillary.

m,n = coefficients associated with flow at the ends of the capillary.

η, ρ = absolute viscosity density of the fluid.

The first term in equation (1) is seen to incorporate the laws determined experimentally by poisenill, while the second or "kinetic energy term", arises from the work done in accelerating and decelerating the fluid at the ends of the capillary. Although it is known that m and n are not constant over the complete range of Reynolds numbers representing the region of laminar flow[132-33], they remain sufficiently constant in some useful ranges to be treated as such.

Capillary viscometers can be broadly grouped as under :

(A) Viscometer for absolute viscosity measurements.

(B) Viscometer for relative viscosity measurements.

  i) Applied pressure viscometers.
  ii) Kinmatic viscometers.

The instrument in section "A" are normally only used for the establishment of primary standards are required very accurate control of applied pressure as well as the precise knowledge of the capillary dimensions.

Type "B" viscometers are those in which measurements are made relative to primary standard liquid (obtained with type (A), or to derived secondary standards. Variable pressure instruments under section "B" (i) typified by the Bingham viscometer use an externally applied pressure to force standard and test liquids through their capillaries.

Kinematic Viscometers:

Some commonly used kinematic viscometer are:

a. cannon - Fenske.
b. British Standard U-tube.
c. Cannon - Fenske for Opaque liquids.
d. Ubbelohde Viscometer.

Perhaps the most widely used type of capillary is one in which the pressure causing flow arises from the hydrostatic head of liquid in the viscometer. In this type of instrument the kinematic viscosity is obtained directly (hence the name kinematic viscometer), and a knowledge of the density of the material under test is required to obtain the absolute viscosity.

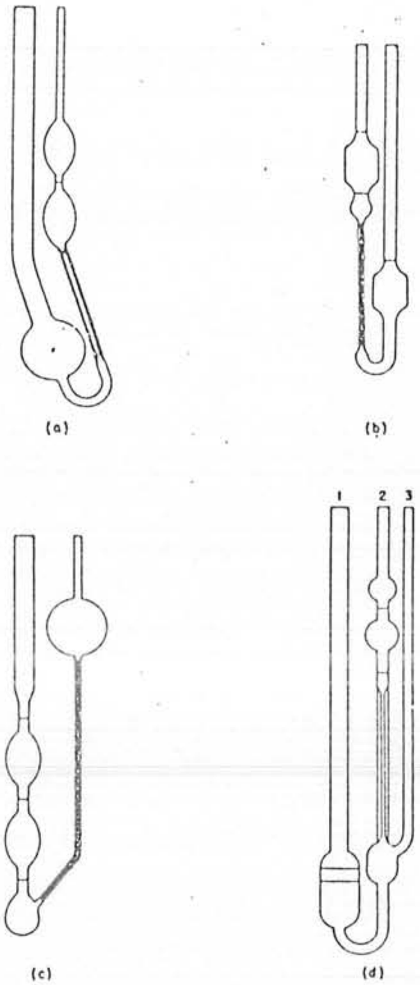


Fig. . Some commonly used kinematic viscometers: (*a*) Cannon-Fenske; (*b*) British standard U-tube; (*c*) Cannon-Fenske for opaque liquids; (*d*) Ubbelohde.

Measurements are made by drawing the liquid up through the capillary into the fiducial bulb, and the time is then measured for it to flow back through the capillary into the lower reservoir. For this case the pressure causing flow is h ρ g, where h is a mean effective value of the head and g is the acceleration of gravity. Substituting h g for P in equation (1). We get

$$\frac{\eta}{\rho} = \frac{\pi r^4 hgt}{8V(1+nr)} - \frac{mV}{8\pi(1+nr)t} \qquad \ldots\ldots (2)$$

$$\frac{\eta}{\rho} = At - B/t \qquad \ldots\ldots (3)$$

$$A = \frac{\pi r^4 hg}{8V(1+nr)} \qquad B = \frac{mV}{8\pi(1+nr)}$$

The constant A and B are commonly evaluated from the measured times of flow for two or more liquids of known viscosity. In many cases it is possible to operate these instrumentsin a range of Reynelds numbers where the second term in the right in equation (3) is negligibly, small and the calculation is simplified accordingly.

An interesting modification of ostwalds, viscometer was developed by Ubbelohde[134], which have been used for measuring the viscosities of acid aqueous solution (i.e. formic, acetic, propanoic and butyric acid in aqueous solution), and that viscometer is called Ubbelohde viscometer. In this instrument tube third is kept closed as the liquid is drawn up in to the fiducial bulb. Before the flow is timed, tube third is opened and the liquid drop away from the end of the capillary, so that during the test the discharge from the capillary drains down the hemispherical surface at the exit end of the capillary. At least two advantages are claimed for this designing viscometer. First, the head is independent of the volume of the charge, because, the liquid has no contact with the lower reservoir and second, the surface forces in the region of the exitof the capillary tend to counterbalance the effect of surface tension in the falling meniscus in the fiducial bulb.

Experimental Errors:

Viscosity is very sensitive property and its determination require skilled and controlled experimentation. The errors are mainly associated with, loading alignment, temperature control and surface tension.

The cannon-Fenske viscometer needs to have very precise loading. Any difference in the volume of the liquid discharging through the instrument will be reflected in the mean driving fluid head. In the Ubbelohde viscometer, however the loading error is practically eliminated, since the mean head is not dependent on the liquid in the lower reservoir but terminates at the junction of the capillary with bulk (middle bulb).

The second end correction, known as the cuette correctio arises when the fluid stream emerges from the capillary, there is a tendency to retain the shape of the capillary upto a finite distance into the fluid medium. This would cause an apparent increase in capillary length.

If the viscometer was not aligned exactly vertical in the bath it may change the hydrostatic head of the fluid. Cannon and Fenske[135] have shown that a change from angle θ to $\theta + d\theta$ in the alignment of the vertical capillary axis produces a change in the fluid head of

$$1 = \frac{\cos(\theta + d\theta)}{\cos\theta}$$

for this to be minimum, angle θ should be zero. An accuracy of 0.1% in the measurement viscosity is consistent with $\theta = 2.5^{\circ}$.

Temperature of the bath should be controlled upto a hundreth of a degree in such precise work; because a change of 0.01°C cause approximately a 0.02% change in the viscosity of water.

In relative measurements an error due to capillary becomes significant if there is a considerable difference between the surface tension of the caliberating fluids and the fluid subsequently tested. The capillarity alter the hydrostatic pressure head of the fluid thus causing a change in flow time. This effect is negligible if the relative measurements corresponds to aqueous solutions, because the surface tension of aqueous solutions of electrolytes change very little with concentration. However, if non aqueous solutions are being caliberated against water the surface tension variation should be taken into account. The Ubbelohde viscometer is reputed to eliminate the surface tension effect by the provision of the suspended level at the top of c which is so designed as to compensate for the forces operating in bulb A.

Thermostating:

The temperature coefficient of the viscosity of water is 2% per degree and if an accuracy of a few hundreth of 1% is desired in the measurement of the relative viscosity of aqueous solution. The measurement must be made in a bath whose temperature can be kept constant to within a hundreth of a degree.

We have used TOWNSON MERCER thermostat which was provided with an electrically driven stirrer, a heating coil, a contact thermometer (i.e. thermoregulator) and a Beckmann thermometer and a support for the viscometer. It held the viscometer firmly and steadly in a perfectly perpendicular position and its construction insured the same position for the viscometer each time when it was placed in the support.

The thermometers were completely immersed so as to avoid any stem exposure correction. The Beckmann thermometer was employed merely as a thermoscope on account of the ease with which it could be read the actual.temperature of the bath. Using such device we were able to control the temperature to one hundreth of a degree.

Preparation of Conductivity Water:

The water was re-distilled in an all glass quickfit apparatus, from the freshly distilled water, with a few crystal of potassium permaganate and a little amount of sodium hydroxide. It was then collected in a little quartz flask.

Chemical Used.

Formic acid E. Merk Art 263, purity = 99%.
Acetic acid E. Merk Art 62 , purity = 96%.
Propionic acid E. Merk, Schucharadt Art 80, purity=99%.
Butyric acid E. Merk, purity = 98%.

Preparation of Solutions.

The solutions were prepared in 100 ml flasks by adding known volume of acids and carefully making up the volume of adding conductivity water in flasks. These were formic, acetic propionic and butyric acids E. Merk . The solutions of each of these acids were prepared in conductivity water at different molar concentratio from 0.1M to 26.95M, 0.1M to 16.95M, 0.1M to 13.23 and 0.1M to 10.6 M respectively.

Density Measurements:

The most common methods of density determination consists in finding the weight of a liquid occuping a known volume defined by the shape of a given volume.

Densities of liquids are most frequently expressed in grams per milliliter. Since the milliliter is defined as one one thousand of the volume of 1 kg of pure ordinary water at its temperature of maximum density (3.98^{O}C).

The densities of liquid were determined by measurements of the weight of a liquid occupying a known volume by pycnometer (Technico) method.

Pycnometer:

Pycnometer are vessels with capillary necks in which a definite volume of liquid is weighed. The pycnometer which hav been used are sprengel ostwald pycnometer (Technico). The pycnometer was cleaned with chromic acid and dried with hot air. The volume of the pycnometer was determined by weighing the vessel (pycnometer) filled with water at a definite temperature. The volume of the pycnometer was calculated from this weight at definite temperature of the bath. from given data of the density of the water at that temperature by using the formula $V = M/d$.

After determining the volume of the pycnometer, the densities of the solutions were measured. The pycnometer was filled with the fluid so that the liquid miniscus is at the marks and it was placed in the thermostat bath for half an hour. The level of the two limbs of the pycnometer was adjusted by drawing out the liquid through absorption in the tissue paper. The pycnometer was removed from the thermostat and wiped and dry with a lintless cloth and the caps placed on the capillary arms. It was allowed to stand on the electrical balance for a few minutes before being weighed. The weight of the liquid was calculated in this way. The densities of the solutions were calculated, (which have prepared at different concentrations)at different temperature from 25°C to 65°C by placing the pycnometer in the thermostat bath.

The Measurements of Time.

The Junghans stop-watch reading 1/10 second was employed in measuring the time of flow of the liquid in the viscometer. The watch was always wound up tightly and then allowed to run for 30 second before being used and was always handled in a systematic manner.

Before taking any reading the liquid was allowed to flow through the capillary twice in order to wet the sides. Five to ten timings were carried out at any one concentration and the extreme variation from the mean was usually about ± 0.1 second.

Viscosity Measurements.

A very fine capillary size viscometer (Ubbelohde) was used for the measurements of viscosities. It was washed with chromic acid and then with distilled water and dried in a vacuume desicator. It is then aligned vertically in the thermostat. A dust free rubber tube was attached to the smaller tube of the viscometer. A specified quantity of conductivity water was added in to viscometer. In the Ubbelohde viscometer tube third was kept closed. Measurements were made by drawing the liquid up through the capillary into fiducial bulb with the help of rubber suction. Viscometer tube third was opened and sucker was also removed. The liquid was then allowed to flow down through the capillary. The stop watch started, when the miniscus passes the upper mark and was stopped when it passes the lower mark and the time was noted. After the measurements with water have been complete. The flow times for a series of other liquids were determined at various temperature, which have been prepared at different concentrations.

CHAPTER - 4

CALCULATIONS AND RESULTS

Densities and viscosities were determined for the binary systems of formic acetic, propionic and butyric acids with water at various temperatures from $25^{\circ}C$ to $65^{\circ}C$ at interval of $5^{\circ}C$ through the following equations.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \qquad \ldots\ldots (1)$$

$$\eta_{rel} = \frac{\eta_2}{\eta_1} = \frac{t_2}{t_1} . \frac{\rho_2}{\rho_1}$$

$$\eta_2 = \frac{t_2}{t_1} . \frac{\rho_2}{\rho_1} . \eta_1 \qquad \ldots\ldots (2)$$

where t_1 and ρ_2 are the flow time and density of mixture, ρ_1, t_1 and η_1 are the density, flow time and viscosity of water. The experimental values for all systems at various temperatures were used to calculate the excess thermodynamic functions and transport properties of binary liquid mixtures with the following equations:

$$V = \frac{X_1M_1 + X_2M_2}{\rho} \qquad \ldots\ldots (3)$$

$$\Delta V^E = \left(\frac{X_1M_1 + X_2M_2}{\rho}\right) - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right) \qquad \ldots\ldots (4)$$

$$\eta^E = \eta - (X_1 \eta_1 + X_2 \eta_2) \qquad \ldots\ldots (5)$$

Here ρ, η, and V are the density, viscosity, and molar volume of the mixture, M_1, M_2, η_1, η_2 are molecular masses, and viscosities of a pure components 1 and 2 respectively and X_1, X_2 represents the mole fraction of water and acid respectively.

The quantity $\frac{\epsilon}{K} = E\eta/R$[79] (E = flow activation energy) was obtained from the slope of the graph for log η against 1/T

$$\eta = A_{exp}\,(E\eta/RT)$$

$$\log\eta = E\eta\ /RT + \log A \qquad \ldots\ldots (6)$$

Various thermodynamic parameters of activation of viscous flow were determined using Eyrings[136] equation. According to Eyring

$$\eta = \frac{hN}{V} \exp\ (\ \Delta H^{\ddagger}\ /RT - \Delta S^{\ddagger}/R) \qquad \ldots\ldots (7)$$

where η is the viscosity of solution, h, N, and V are Plank's constant, Avogadro's number, and molar volume, respectively.

When $\ln(\eta V/hN)$ is plotted against 1/T, the slope is equal to $\Delta H^{\ddagger}/R$ and the intercept is equal to $-\Delta S^{\ddagger}/R$. Using graphical method, the activation parameters $\Delta H^{\ddagger}$, (the enthalpy change for activation process) and $\Delta S^{\ddagger}$, (the entropy change for activation process) were obtained and $\Delta G^{\ddagger}$, (standard free energy of activation for viscous flow) was obtained using the equation:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \ldots\ldots (8)$$

Values obtained are presented in Table

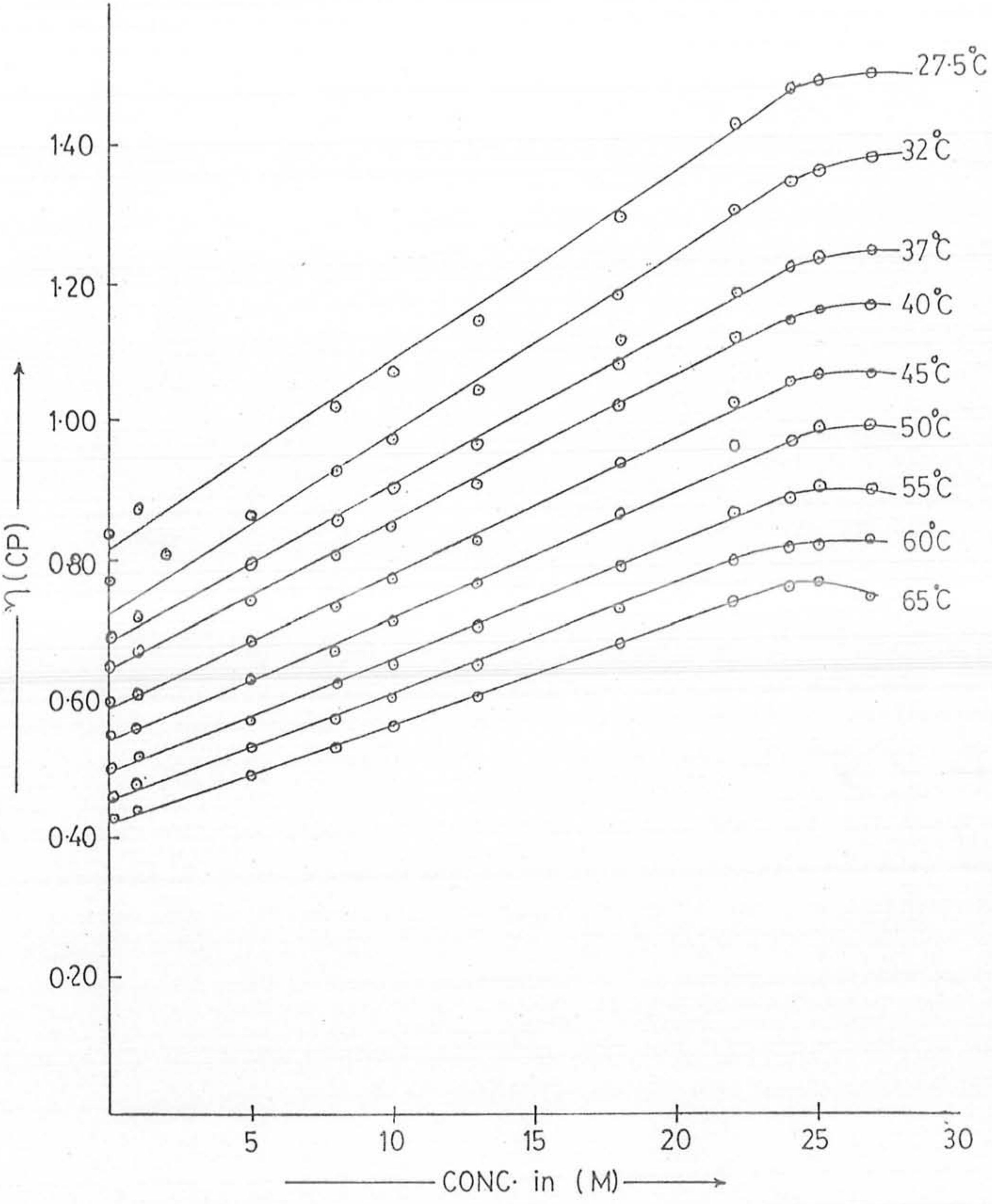


FIGURE 1. RELATIVE VISCOSITY (CP)-CONCENTRATION CURVES FOR FORMIC ACID IN WATER.

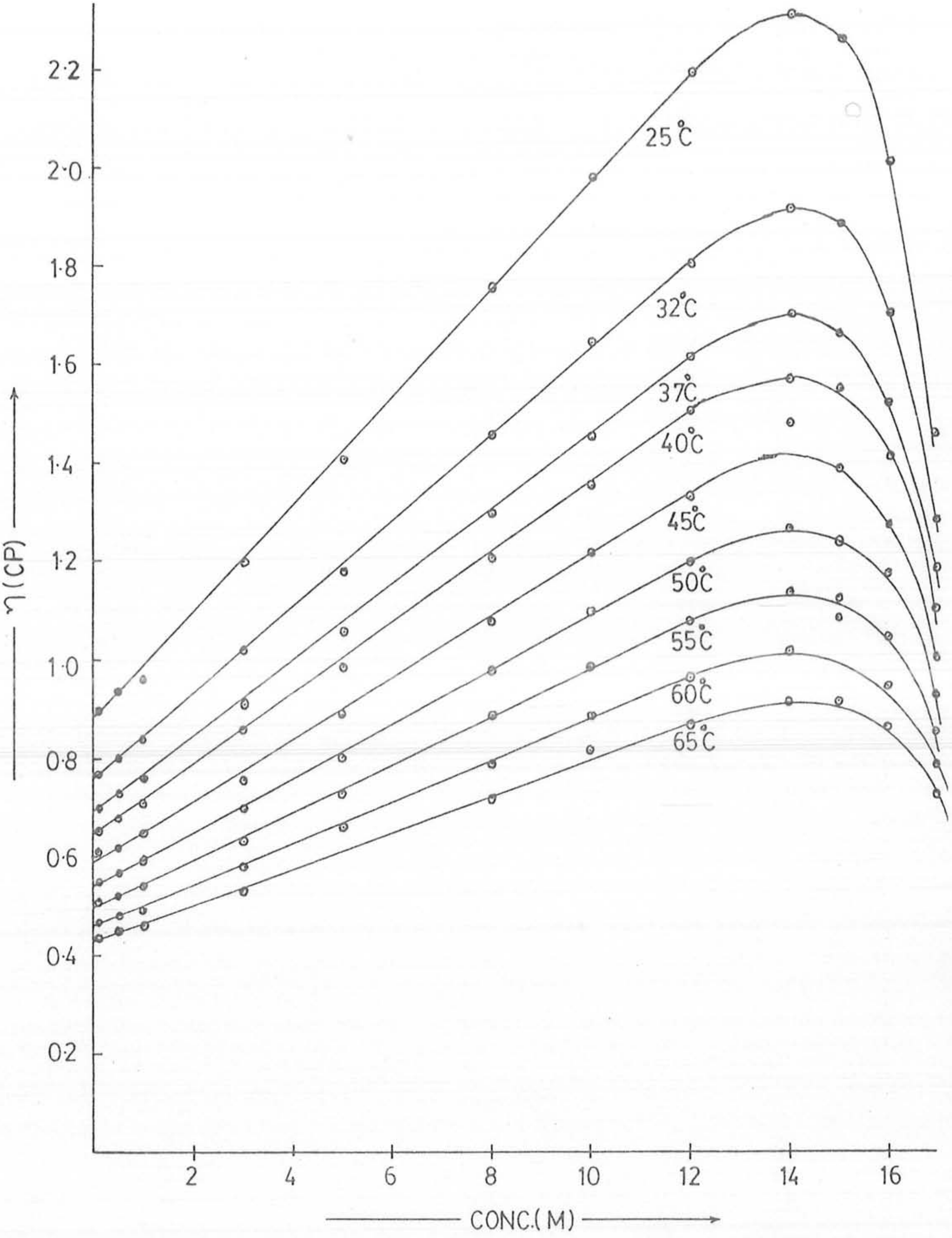


FIGURE 2. RELATIVE VISCOSITY (CP)-CONCENTRATION CURVES FOR ACETIC ACID IN WATER.

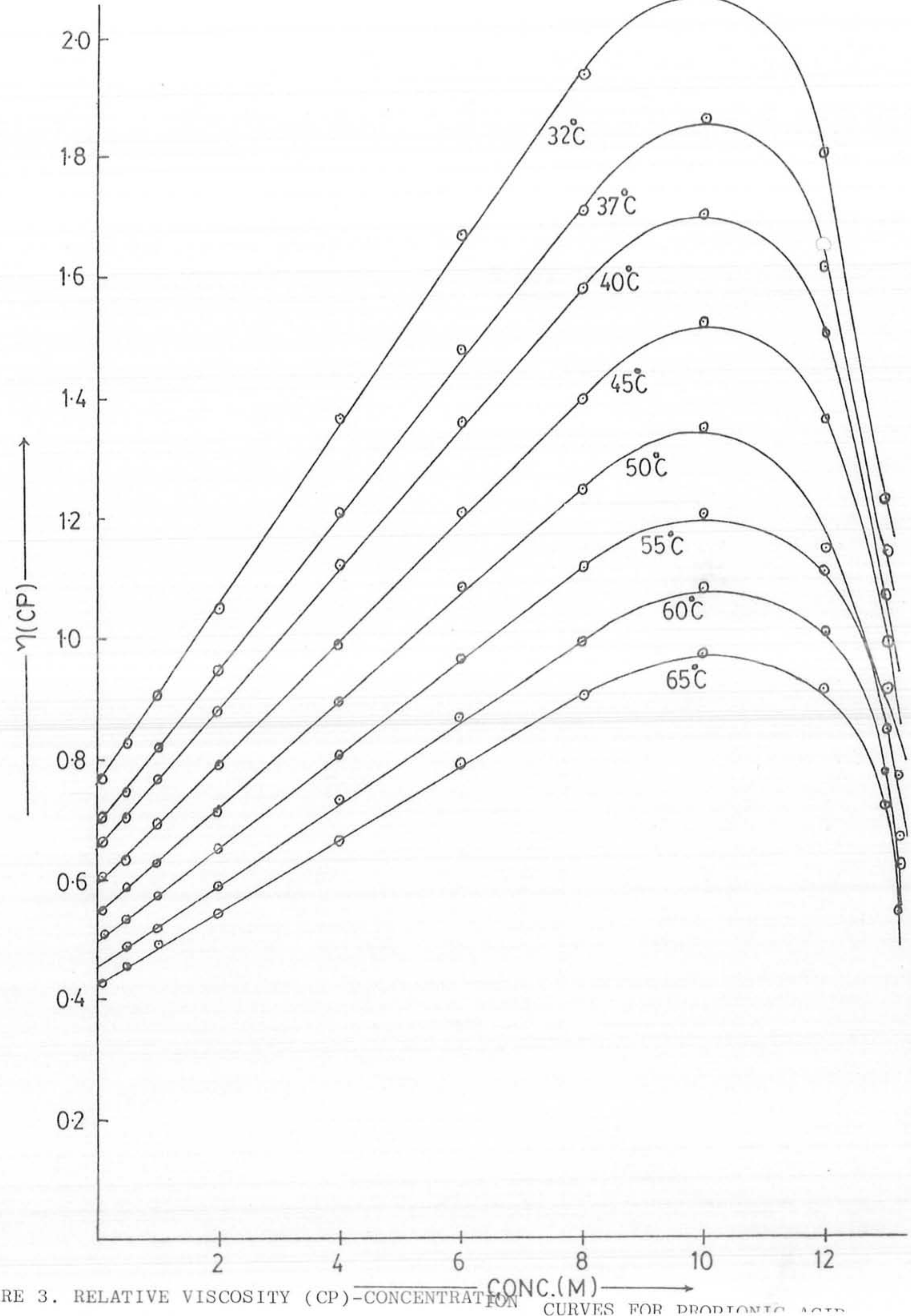


FIGURE 3. RELATIVE VISCOSITY (CP)-CONCENTRATION CURVES FOR PROPIONIC ACID

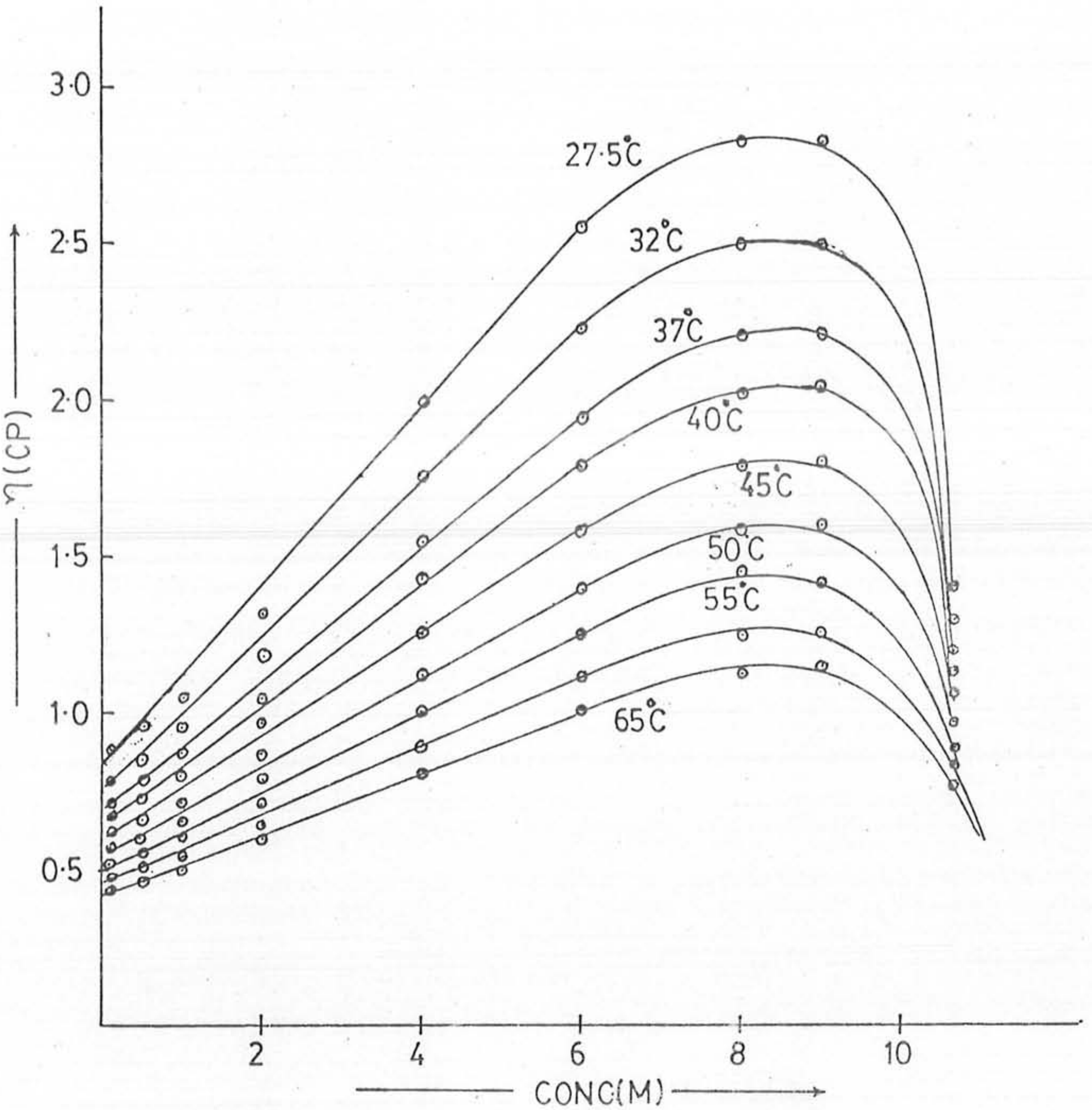


FIGURE 4. RELATIVE VISCOSITY (CP)-CONCENTRATION CURVES FOR BUTYRIC ACID IN WATER.

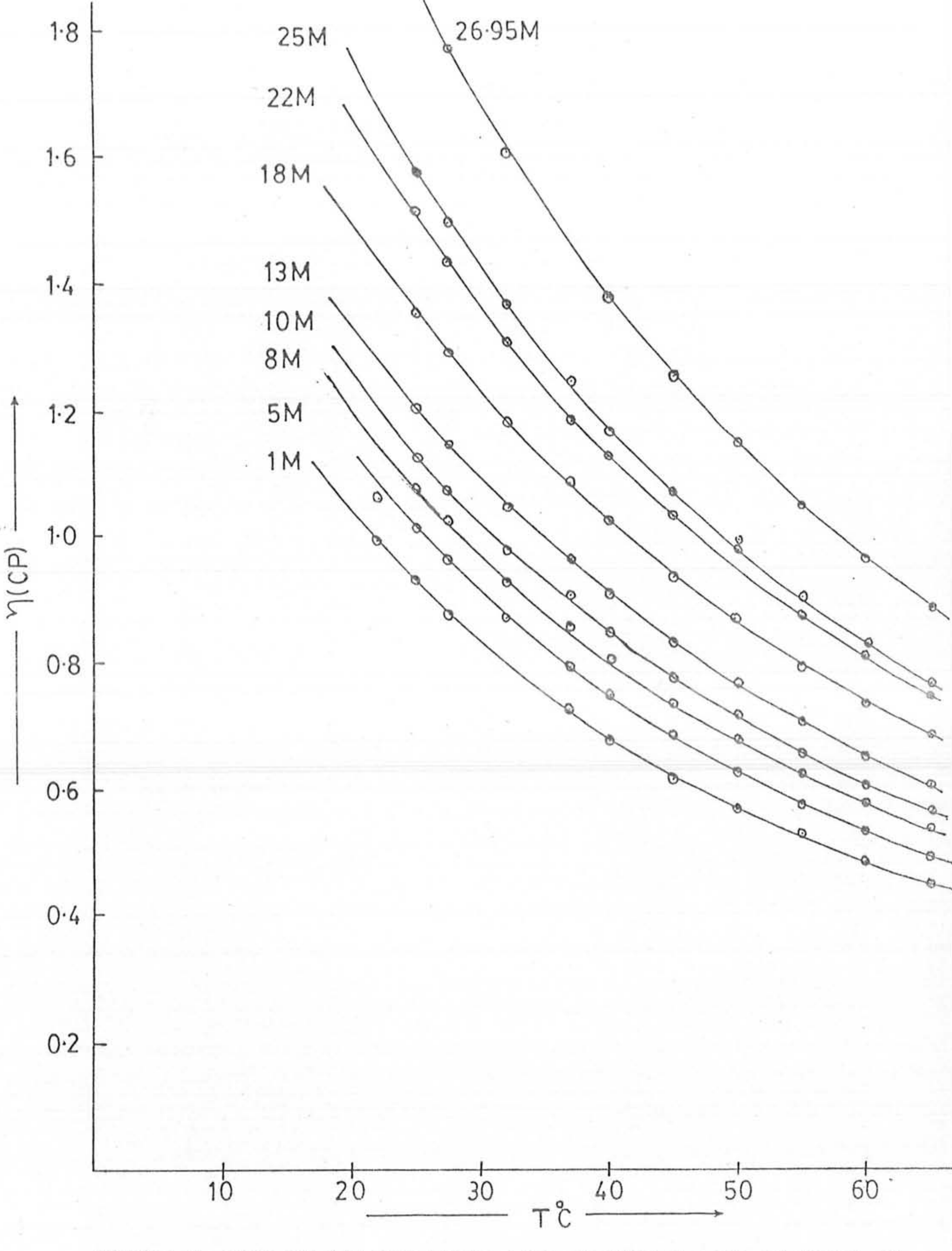


FIGURE 5. PLOT OF THE VISCOSITY (CP) OF FORMIC ACID IN WATER VS. THE TEMPERATURE IN ^{o}C.

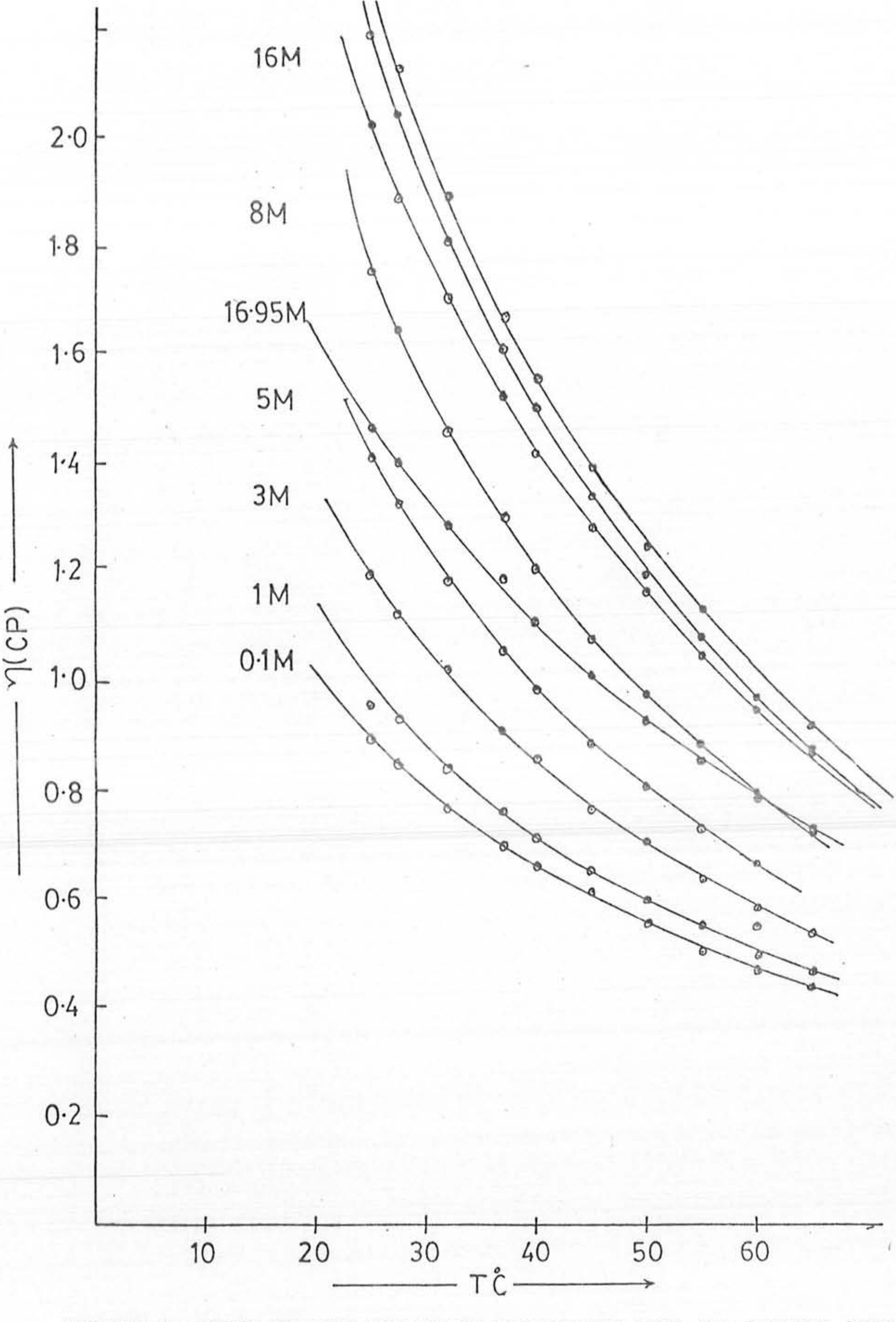


FIGURE 6. PLOT OF THE RELATIVE VISCOSITY (CP) OF ACETIC ACID IN WATER VS. THE TEMPERATURE IN ^{o}C.

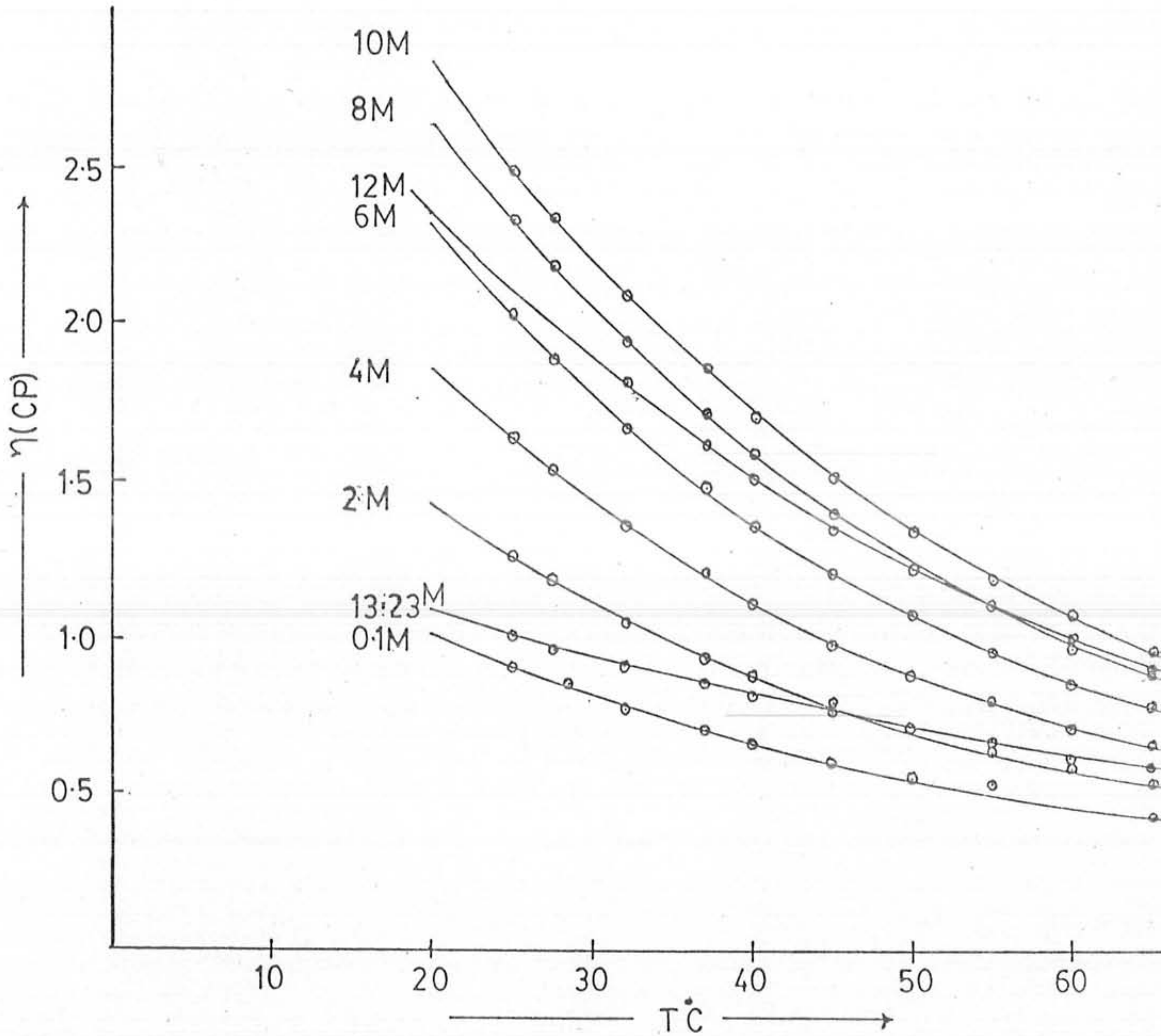


FIGURE 7. PLOT OF THE RELATIVE VISCOSITY (CP) OF PROPIONIC ACID IN WATER VS. THE TEMPERATURE IN °C.

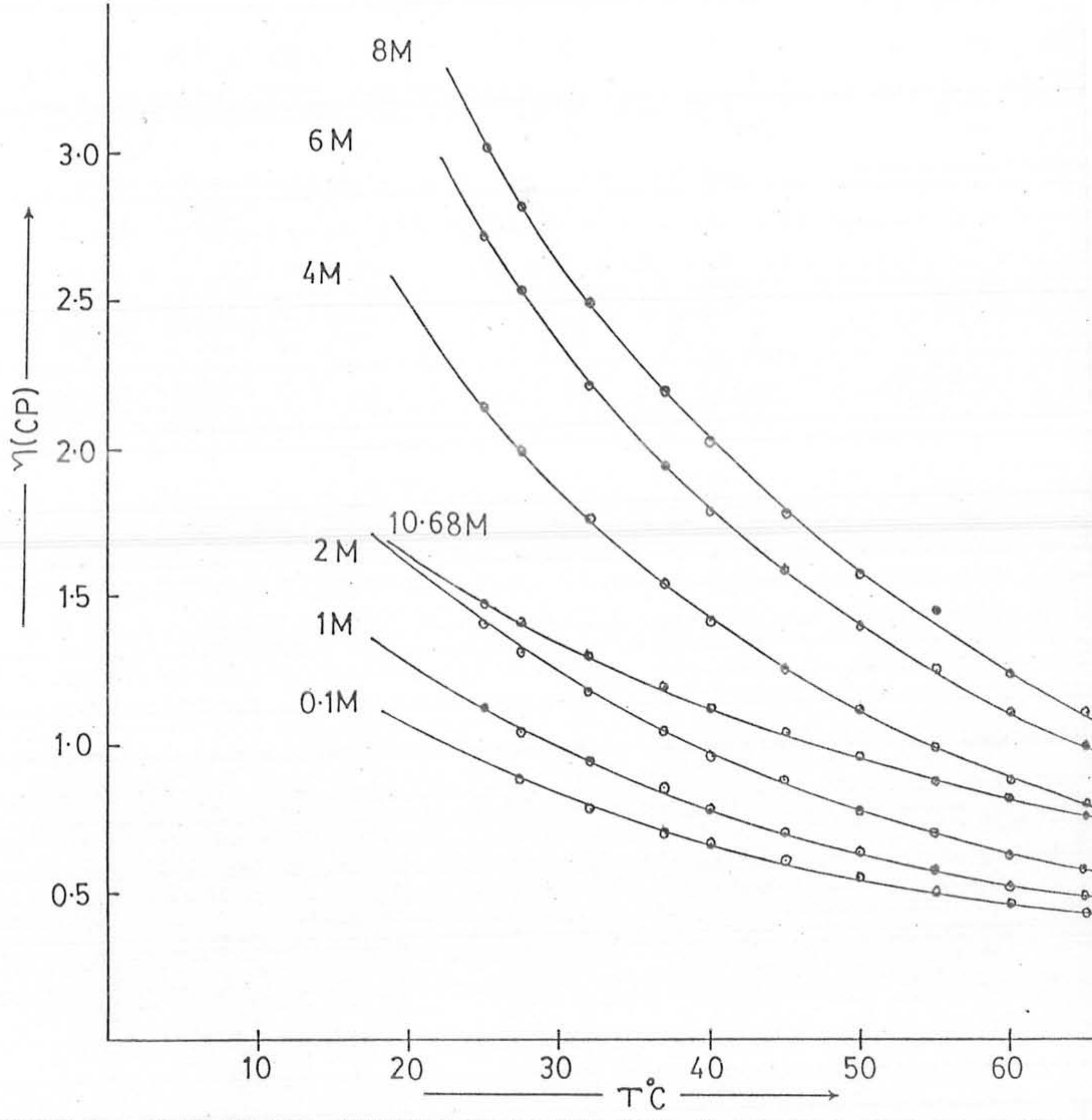


FIGURE 8. PLOT OF THE RELATIVE VISCOSITY (CP) OF BUTYRIC ACID IN WATER VS. THE TEMPERATURE IN °C.

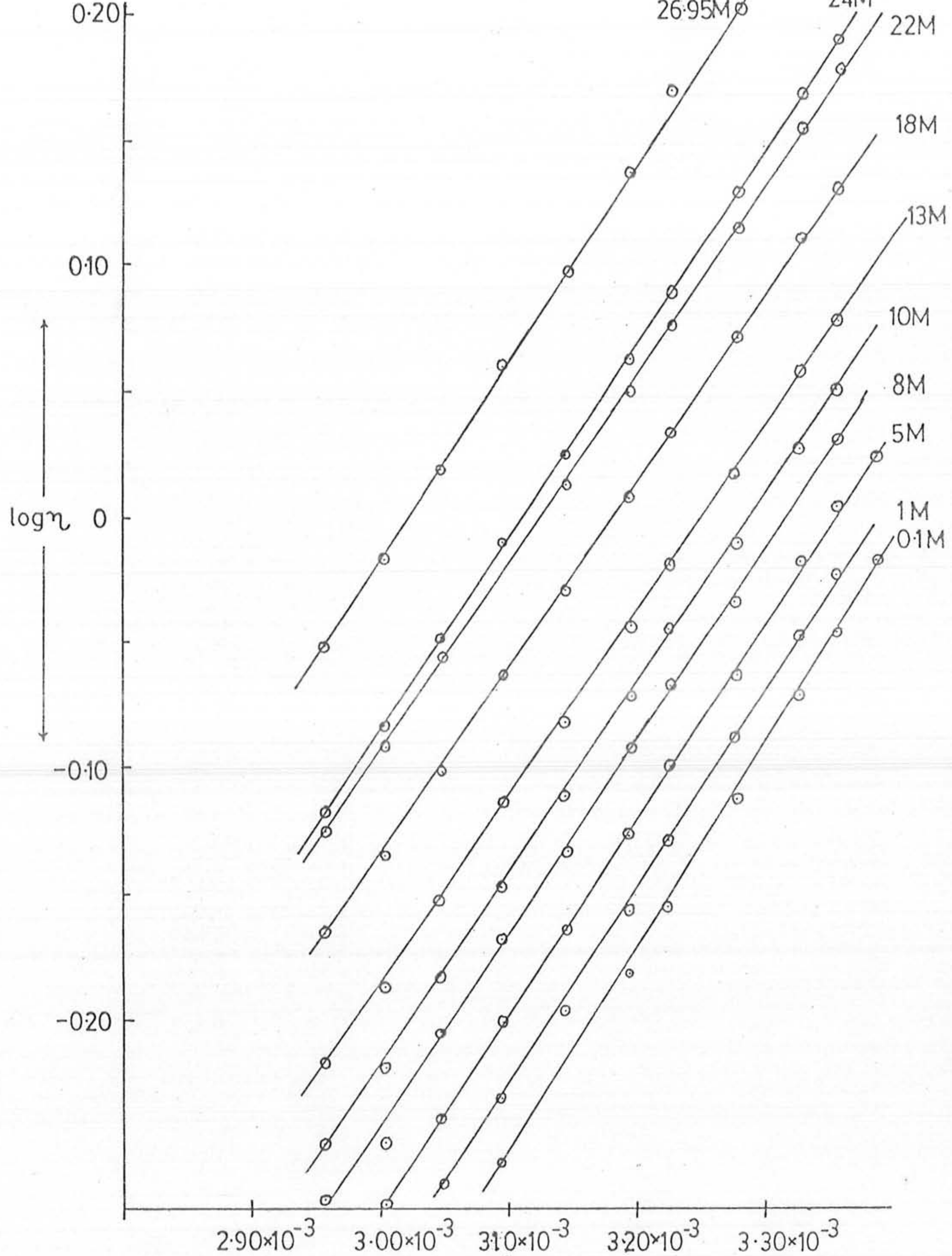


FIGURE 9. PLOT OF THE LOG OF VISCOSITY OF FORMIC ACID IN WATER VS. THE RECIPROCAL OF THE ABSOLUTE TEMPERATURE.

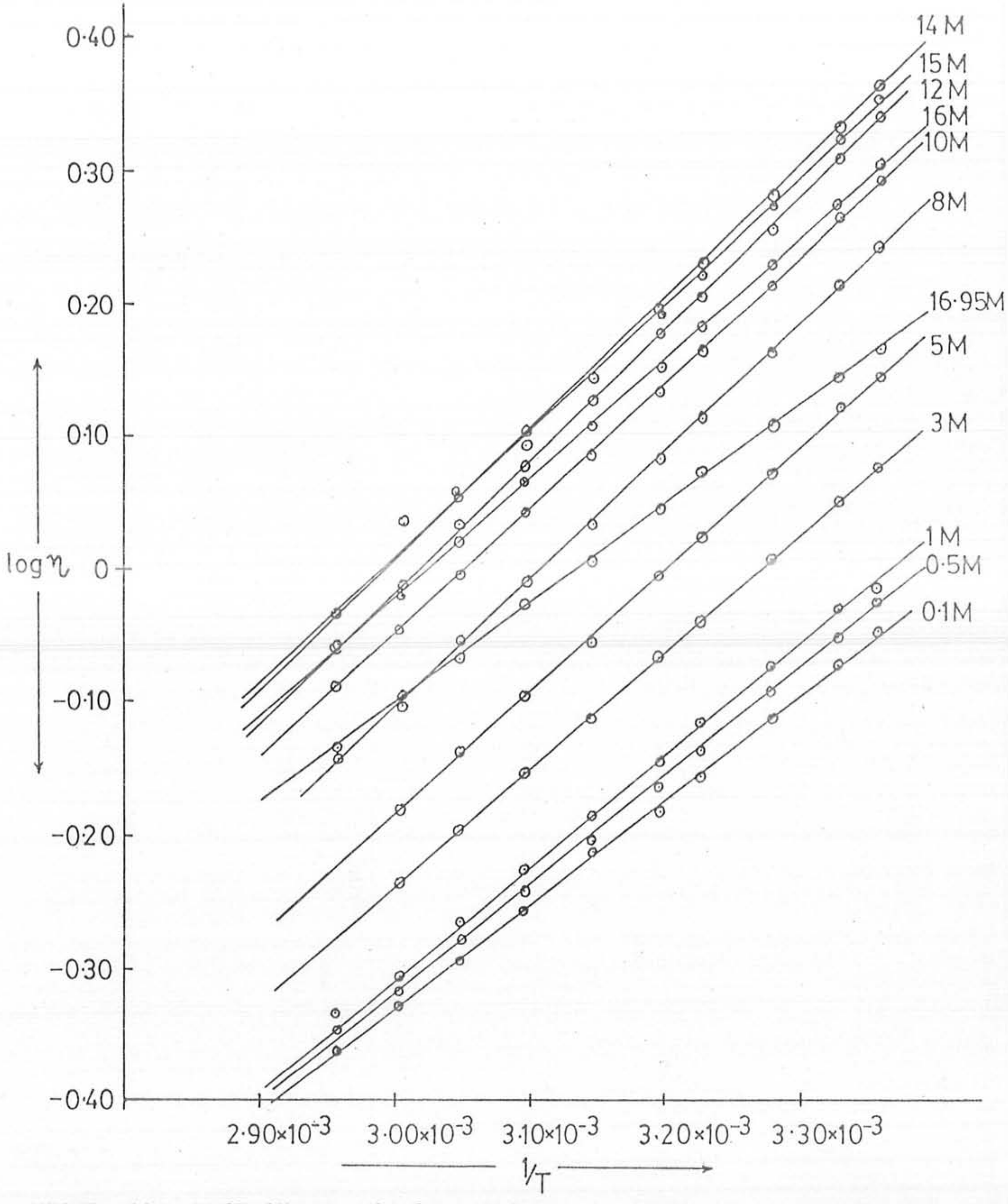


FIGURE 10. PLOT OF THE LOG OF VISCOSITY OF ACETIC ACID IN WATER VS. THE RECIPROCAL OF THE ABSOLUTE TEMPERATURÉ.

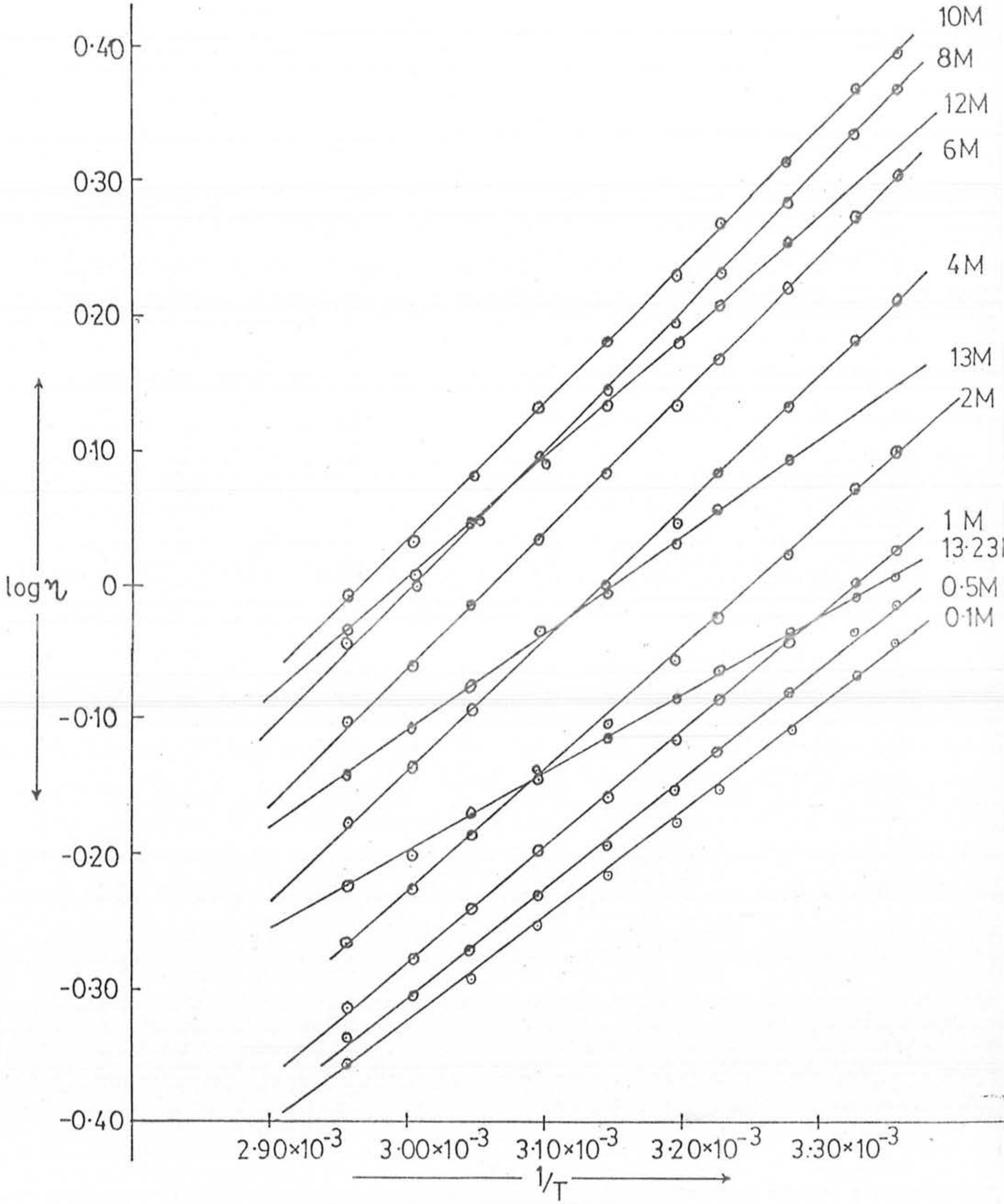


FIGURE 11. PLOT OF THE LOG OF VISCOSITY OF PROPIONIC ACID IN WATER VS. THE RECIPROCAL OF THE ABSOLUTE TEMPERATURE.

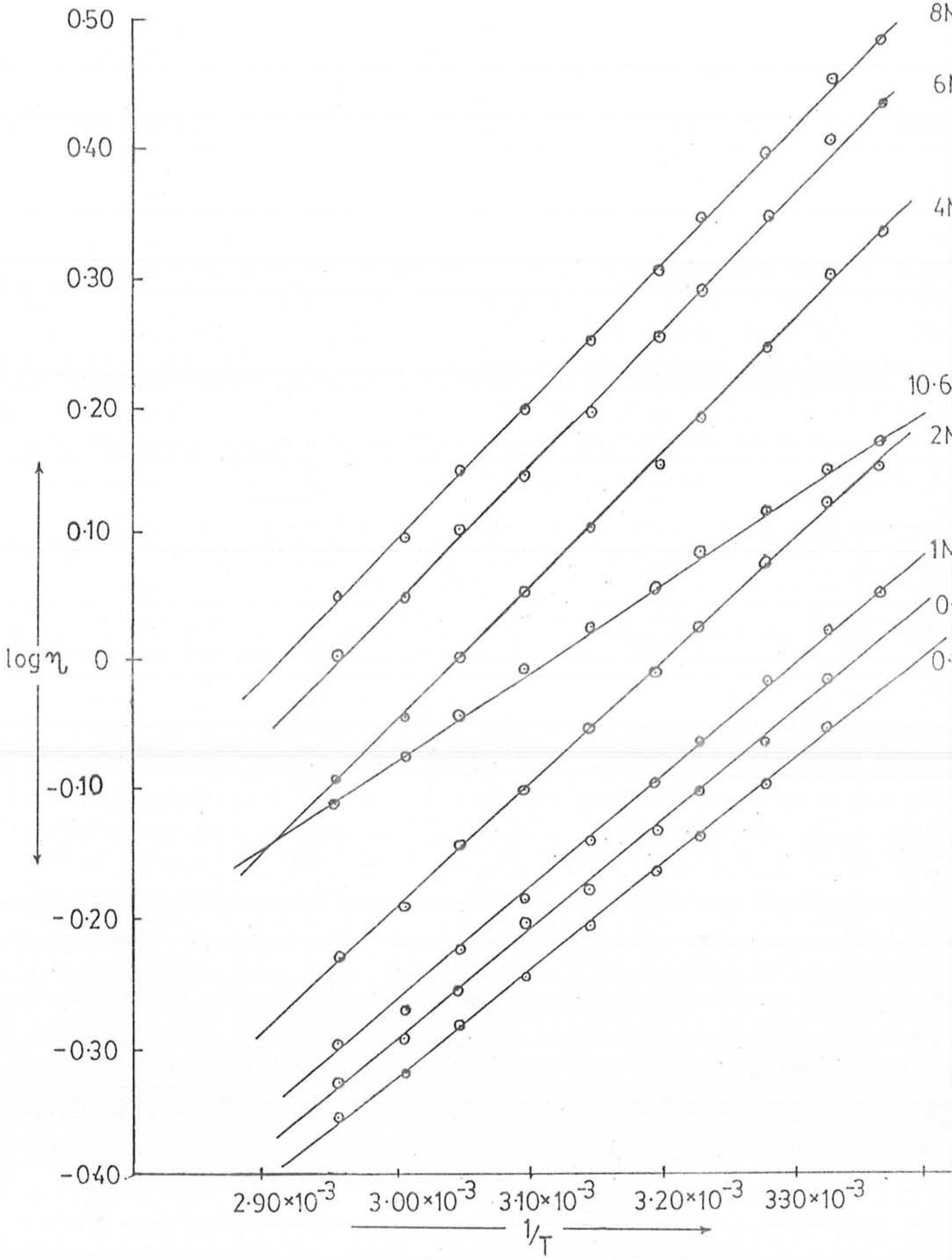


FIGURE 12. PLOT OF THE LOG OF VISCOSITY OF BUTYRIC ACID IN WATER VS. TH
RECIPROCAL OF THE ABSOLUTE TEMPERATURE.

TABLE - 1.

FLOW ACTIVATION ENERGY FOR CARBOXYLIC ACIDS.

S. No.	Conc. of Formic Acid.(M.)	E_η for Formic Acid.	Conc. of Acetic Acid.(M)	E_η for Acetic Acid.	Conc. of Propionic Acid.(M)	E_η for Pripionic Acid.	Conc. of Propionic Acid (M)	E_η for Butyric Acid
1.	0.1	1436.04	0.1	1464.19	0.1	1531.77	0.1	1595.61
2.	1	1464.19	0.5	1495.87	0.5	1595.61	0.5	1641.19
3.	5	1464.19	1	1542.41	1	1441.19	1	1675.39
4.	8	1464.19	3	1650.62	2	1777.94	2	1740.65
5.	10	1453.76	5	1679.55	4	1886.13	4	1971.87
6.	13	1436.04	8	1804.25	6	1914.71	6	2030.76
7.	18	1436.04	10	1736.60	8	1994.49	8	2083.04
8.	22	1436.08	12	1884.32	10	1914.71	10.68	1367.66
9.	24	1436.04	14	1914.71	12	1718.34	-	-
10.	26.95	1456.84	15	1858.94	13	1367.66	-	-
11.	-	-	16	1823.54	13.23	1148.83	-	-
12.	-	-	16.95	1436.04	-	-	-	-

Flow Activation Energies (E_η) are in J mol^{-1}.

TABLE - 2.

Excess Viscosity (η^E) and Excess Volume (ΔV^E) of Binary Liquid Mixture at 25°C.

S. No.	Mol. Frac.of Formic Acid-X_2	Formic Acid+ Water System		Mol. Frac.of Acetic Acid.X_2	Acetic Acid+ Water System		Mol. Frac.of Propanoic Acid.X_2	Propionic Acid+ Water System		Mol. Frac.of Butyric Acid.X_2	Butyric Acid+ Water System	
		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)
1.	0.002	0.007	-0.028	0.002	0.006	-0.036	0.002	0.019	-0.052	-	-	-
2.	0.009	0.019	-0.053	0.009	0.044	-0.072	0.009	0.080	-0.107	-	-	-
3.	0.018	0.021	-0.089	0.019	0.062	-0.138	0.019	0.174	-0.025	0.194	0.229	-0.203
4.	0.037	0.035	-0.128	0.061	0.273	-0.311	0.041	0.461	-0.319	0.042	0.508	-0.328
5.	0.099	0.054	-0.249	0.111	0.455	-0.498	0.093	0.746	-0.571	0.102	1.207	-0.504
6.	0.171	0.007	0.336	0.208	0.745	-0.728	0.164	1.119	-0.806	0.194	1.718	-0.712
7.	0.224	0.081	0.402	0.292	0.924	-0.844	0.263	1.421	-1.026	0.350	1.930	-0.950
8.	0.314	0.098	-0.434	0.400	1.076	-0.946	0.415	1.563	-1.220	0.681	1.729	-1.573
9.	0.500	0.124	-0.425	0.544	1.110	-0.953	0.949	0.007	+0.006	0.897	0.062	+0.084
10.	0.695	0.144	-0.385	0.636	1.009	-0.843	-	-	-	-	-	-
11.	0.813	0.109	-0.299	0.745	0.699	-0.625	-	-	-	-	-	-
12.	0.879	0.081	-0.235	0.871	0.075	-0.124	-	-	-	-	-	-
13.	0.968	0.021	-0.101	-	-	-	-	-	-	-	-	-

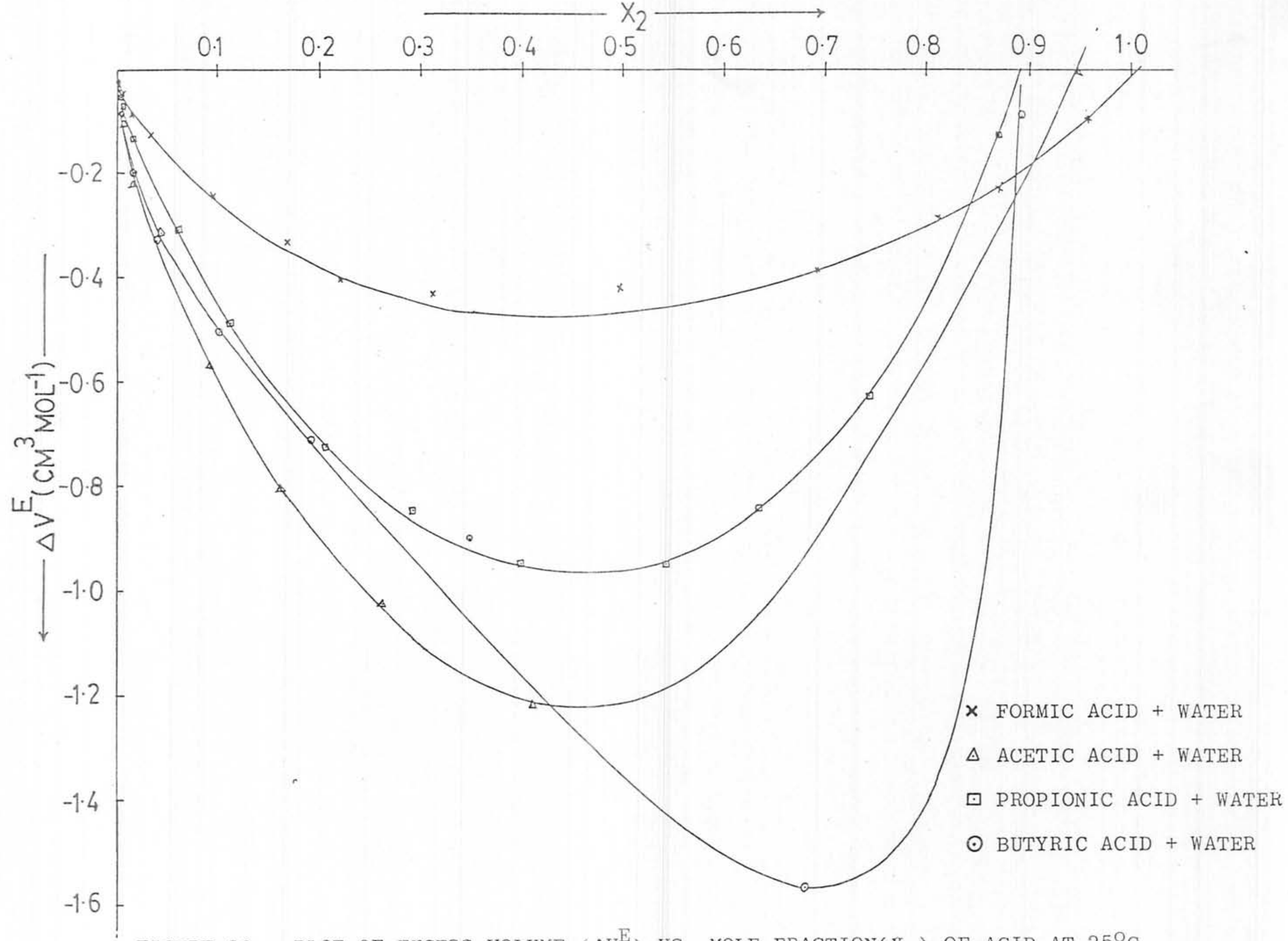


FIGURE 20. PLOT OF EXCESS VOLUME (ΔV^E) VS. MOLE FRACTION(X_2) OF ACID AT 25°C.

TABLE - 3.

Excess Viscosity (η^E) and Excess Volume (ΔV^E) of Binary Liquid Mixture at 32°C.

S. No.	Mol. Frac. of Formic Acid-X_2	Formic Acid+ Water System		Mol. Frac. of Acetic Acid. X_2	Acetic Acid+ Water System		Mol. Frac. of Propanoic Acid. X_2	Propionic Acid+ Water System		Mol. Frac. of Butyric Acid. X_2	Butyric Acid+ Water System	
		η^E (cp)	ΔV^E (cm^{3}mol^{-1})		η^E (cp)	ΔV^E (cm^{3}mol^{-1})		η^E (cp)	ΔV_1^E (cm^{3}mol^{-1})		η^E (cp)	ΔV^E (cm^3 mol^{-1})
1.	0.002	0.006	-0.009	0.002	0.002	-0.007	0.002	0.013	-0.052	0.002	0.029	-0.044
2.	0.009	0.010	-0.035	0.009	0.034	-0.079	0.009	0.062	-0.107	0.009	0.089	-0.117
3.	0.018	0.015	-0.015	0.019	0.067	-0.134	0.019	0.139	-0.233	0.019	0.179	-0.193
4.	0.038		-0.136	0.061	0.224	-0.312	0.041	0.283	-0.314	0.042	0.399	-0.334
5.	0.099	0.038	-0.257	0.111	0.296	-0.474	0.093	0.587	-0.561	0.102	0.944	-0.499
6.	0.171	0.055	-0.312	0.208	0.589	-0.713	0.163	0.882	-0.795	0.193	1.358	-0.699
7.	0.224	0.076	-0.375	0.292	0.732	-0.838	0.263	1.144	-1.019	0.314	1.546	-0.939
8.	0.313	0.086	-0.421	0.399	0.842	-0.921	0.414	1.255	-1.221	0.676	1.370	-1.603
9.	0.499	0.110	-0.424	0.542	0.873	-0.928	0.670	0.943	-1.169	0.888	0.061	+0.100
10.	0.693	0.114	-0.376	0.633	0.799	-0.835	0.880	0.334	-0.589	-	-	-
11.	0.811	0.084	-0.309	0.741	0.556	-0.638	0.941	0.009	+0.013	-	-	-
12.	0.876	0.056	-0.237	0.866	0.070	-0.117	-	-	-	-	-	-
13.	0.965	0.217	-0.111	-	-	-	-	-	-	-	-	-

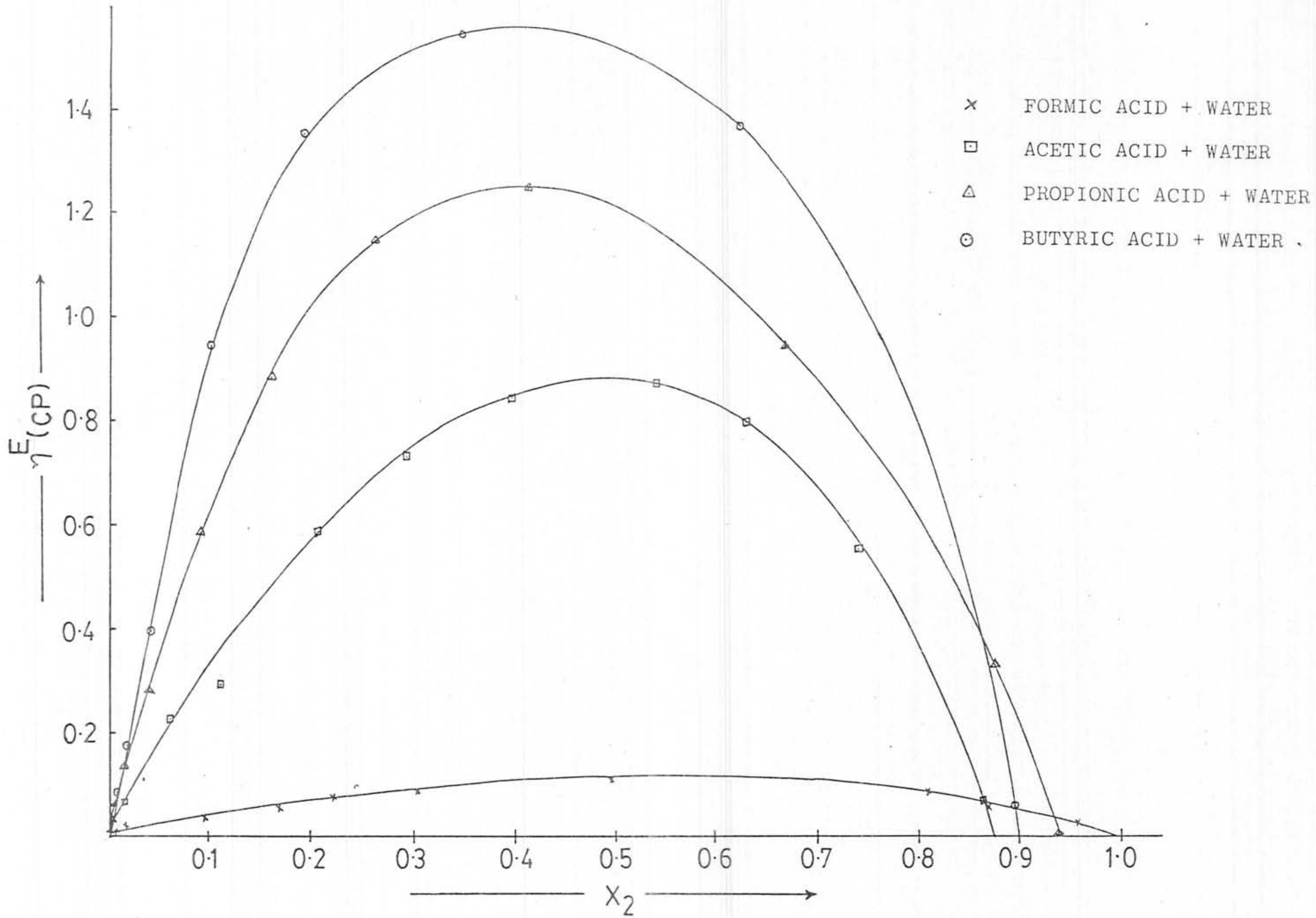


FIGURE 13. PLOT OF EXCESS VISCOSITY (η^E) VS. MOLE FRACTION OF ACID AT 32°C.

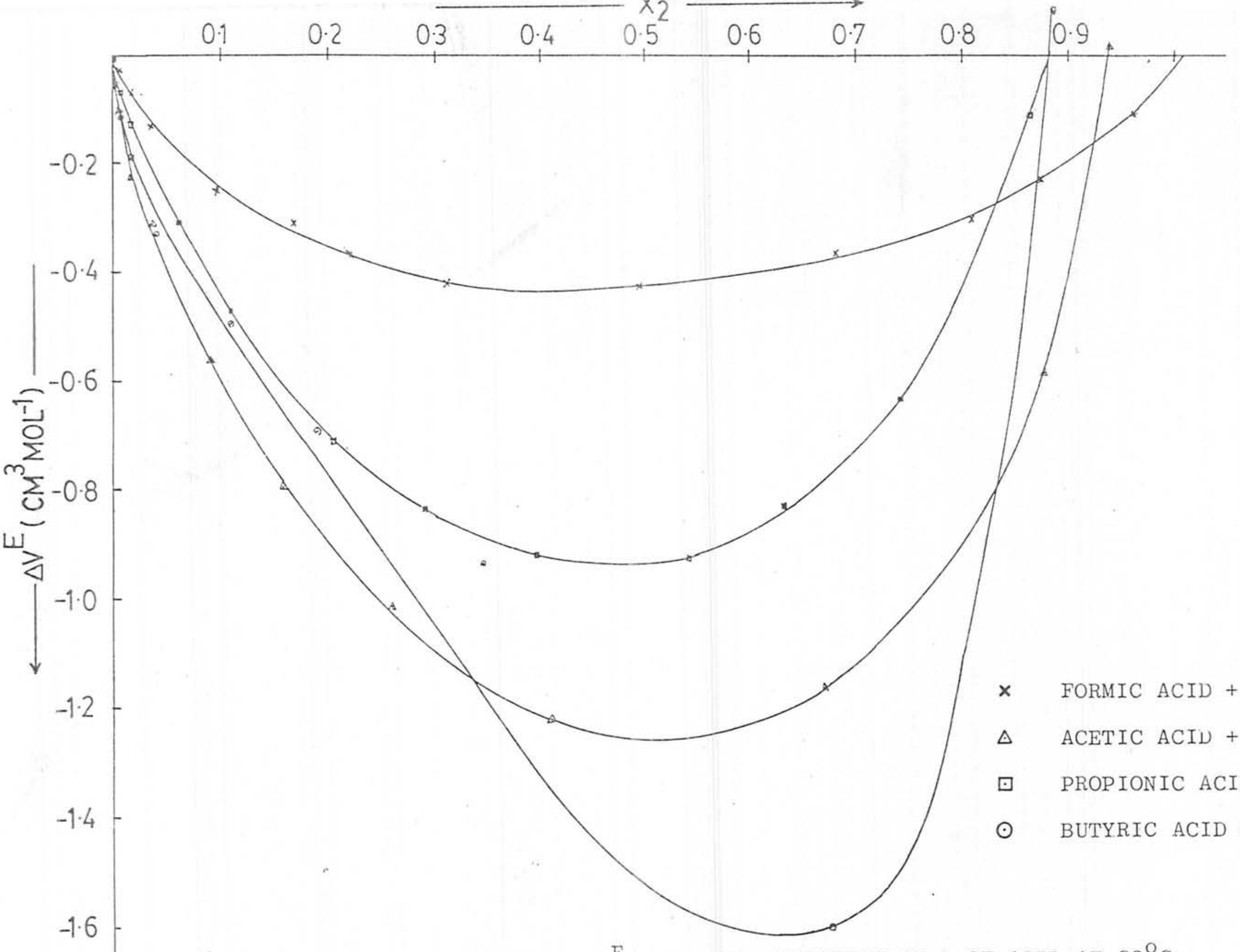


FIGURE 21. PLOT OF EXCESS VOLUME (ΔV^E) VS. MOLE FRACTION (X_2) OF ACID AT 32°C.

TABLE - 4.

Excess Viscosity (η^E) and Excess Volume (ΔV^E) of Binary Liquid Mixture at 40°C...

S. No.	Mol. Frac. of Formic Acid-X_2	Formic Acid+ Water System		Mol. Frac. of Acetic Acid. X_2	Acetic Acid+ Water System		Mol. Frac. of Propanoic Acid. X_2	Propionic Acid+ Water System		Mol. Frac. of Butyric Acid. X_2	Butyric Acid+ Water System	
		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)
1.	0.002	0.004	-0.012	0.002	0.003	-0.044	0.002	0.011	-0.062	0.002	0.024	-0.059
2.	0.009	0.012	-0.043	0.009	0.026	-0.078	0.009	0.050	-0.111	0.009	0.071	-0.119
3.	0.018	0.017	-0.081	0.019	0.051	-0.119	0.019	0.109	-0.236	0.018	0.138	-0.191
4.	0.038	0.025	-0.119	0.061	0.175	-0.307	0.041	0.221	-0.307	0.042	0.302	-0.307
5.	0.100	0.042	-0.236	0.111	0.282	-0.467	0.093	0.452	-0.554	0.102	0.726	-0.487
6.	0.171	0.064	-0.299	0.207	0.261	-0.699	0.163	0.678	-0.786	0.193	1.004	-0.701
7.	0.223	0.078	-0.364	0.291	0.569	-0.832	0.261	0.882	-1.015	0.347	1.207	-0.951
8.	0.313	0.089	-0.399	0.398	0.674	-0.914	0.412	0.982	-1.220	0.670	1.069	-1.649
9.	0.497	0.108	-0.416	0.539	0.681	-0.917	0.666	0.751	-1.159	0.877	0.060	+0.125
10.	0.689	0.112	-0.385	0.629	0.624	-0.832	0.871	0.274	-0.611	-	-	-
11.	0.807	0.082	-0.307	0.736	0.435	-0.604	0.931	0.012	+0.023	-	-	-
12.	0.872	0.059	-0.250	0.859	0.064	-0.109	-	-	-	-	-	-
13.	0.959	0.021	-0.125	-	-	-	-	-	-	-	-	-

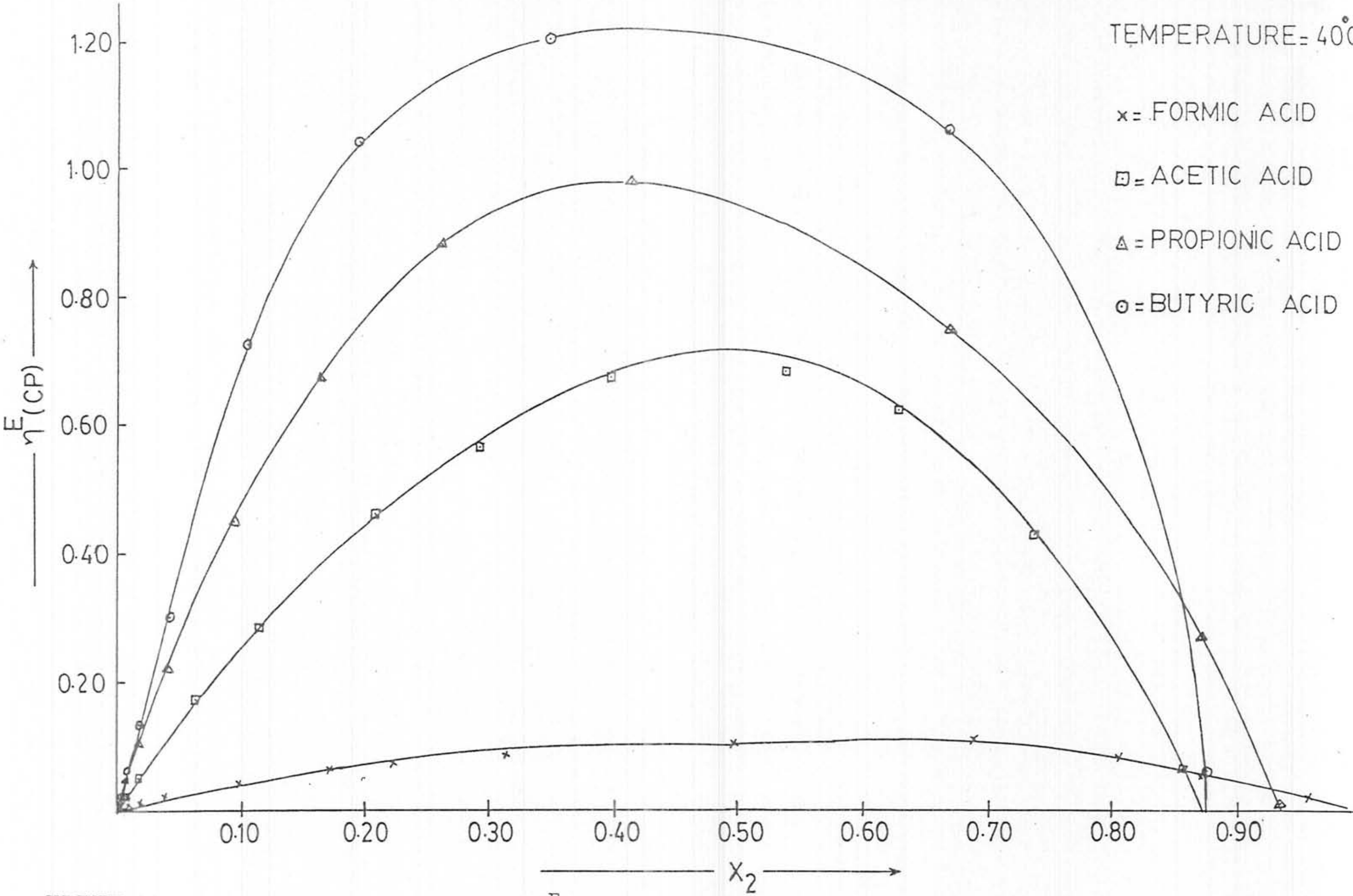


FIGURE 14. PLOT OF EXCESS VISCOSITY (η^E) VS. MOLE FRACTION OF ACID AT 40°C.

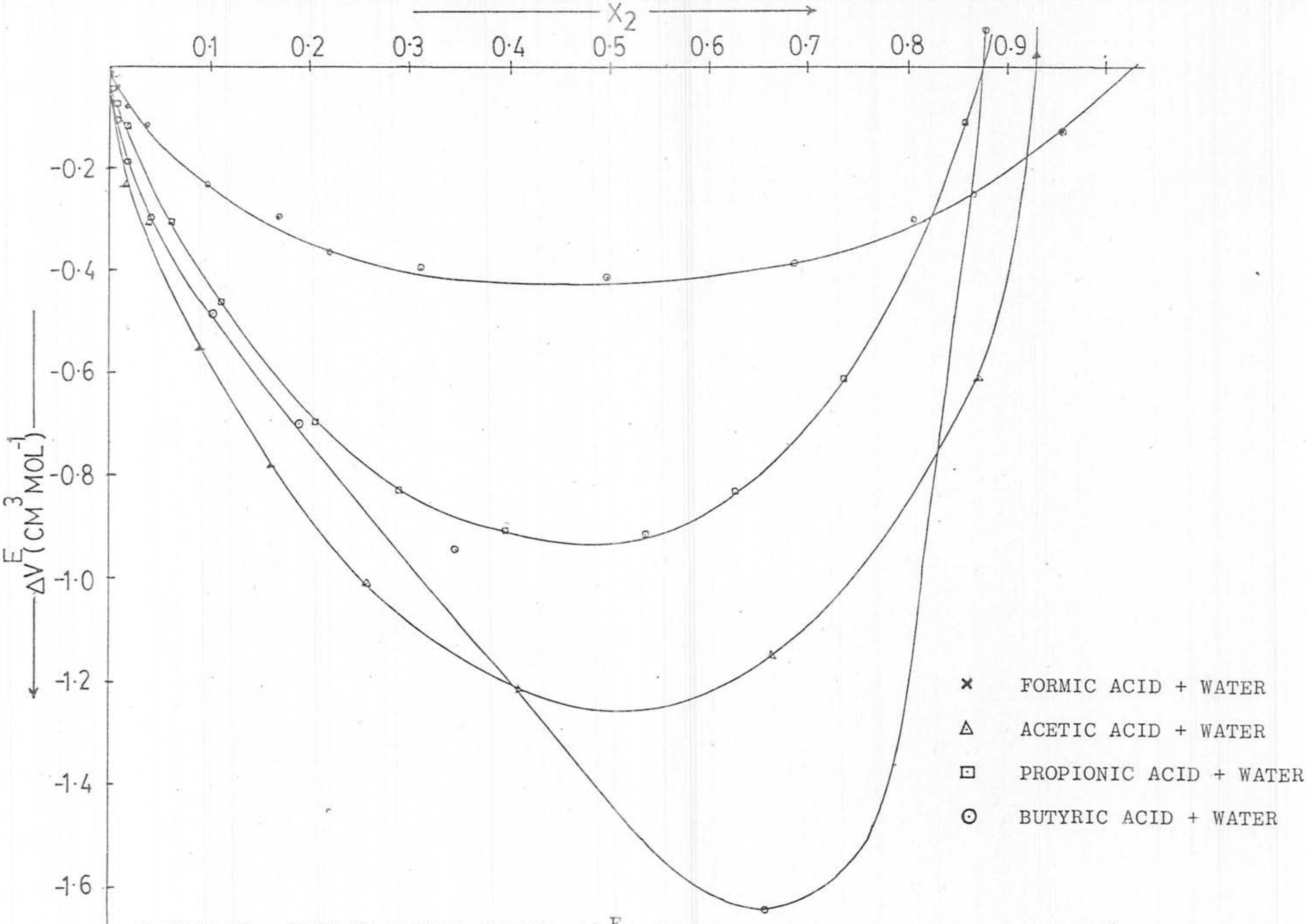


FIGURE 22. PLOT OF EXCESS VOLUME (ΔV^E) VS. MOLE FRACTION (X_2) OF ACID AT 40°C.

TABLE - 5.

Excess Viscosity (η^E) and Excess Volume (ΔV^E) of Binary Liquid Mixture at 45°C.

S. No.	Mol. Frac. of Formic Acid-X_2	Formic Acid+ Water System		Mol. Frac. of Acetic Acid. X_2	Acetic Acid+ Water System		Mol. Frac. of Propanoic Acid. X_2	Propionic Acid+ Water System		Mol. Frac. of Butyric Acid. X_2	Butyric Acid+ Water System	
		η^E (cp)	ΔV^E ($cm3mol^{-1}$)		η^E (cp)	ΔV^E (cm^3mol^{-1})		η^E (cp)	ΔV^E cm^3 mol^{-1}		η^E (cp)	ΔV^E (cm^3mol^{-1})
1.	0.002	0.003	-0.007	0.002	0.013	-0.041	0.002	0.011	-0.066	0.002	0.021	-0.026
2.	0.009	0.009	-0.043	0.009	0.021	-0.092	0.009	0.040	-0.109	0.009	0.059	-0.123
3.	0.018	0.014	-0.037	0.019	0.045	-0.121	0.019	0.095	-0.234	0.019	0.134	-0.199
4.	0.371	0.022	-0.119	0.061	0.149	-0.305	0.041	0.187	-0.307	0.042	0.261	-0.300
5.	0.099	0.041	-0.230	0.111	0.243	-0.465	0.093	0.384	-0.542	0.102	0.619	-0.479
6.	0.170	0.058	-0.291	0.207	0.399	-0.697	0.163	0.693	-0.769	0.192	0.899	-0.692
7.	0.223	0.071	-0.349	0.290	0.504	-0.825	0.261	0.759	-1.127	0.346	1.168	-0.930
8.	0.312	0.084	-0.388	0.397	0.579	-0.922	0.410	0.859	-1.216	0.067	1.138	-1.641
9.	0.496	0.104	-0.404	0.538	0.551	-0.936	0.661	0.653	-1.164	0.869	0.061	+0.140
10.	0.688	0.109	-0.372	0.627	0.539	-0.844	0.861	0.245	-0.593	-	-	-
11.	0.804	0.080	-0.299	0.733	0.382	-0.625	0.924	0.013	+0.031	-	-	-
12.	0.869	0.058	-0.252	0.854	0.061	-0.104	-	-	-	-	-	-
13.	0.956	0.021	-0.136	-	-	-	-	-	-	-	-	-

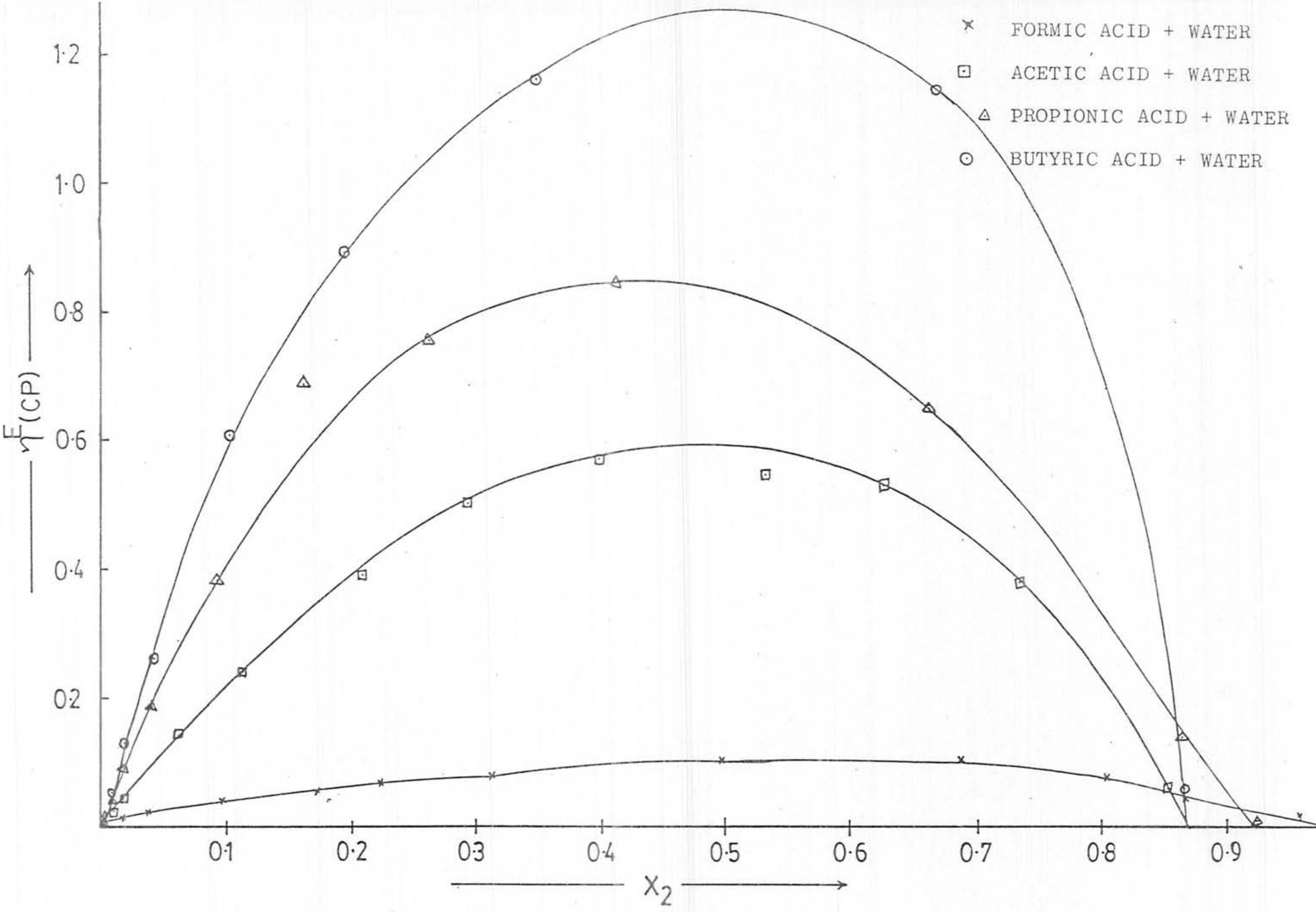


FIGURE 15. PLOT OF EXCESS VISCOSITY (η^E) VS. MOLE FRACTION OF ACID AT 45°C.

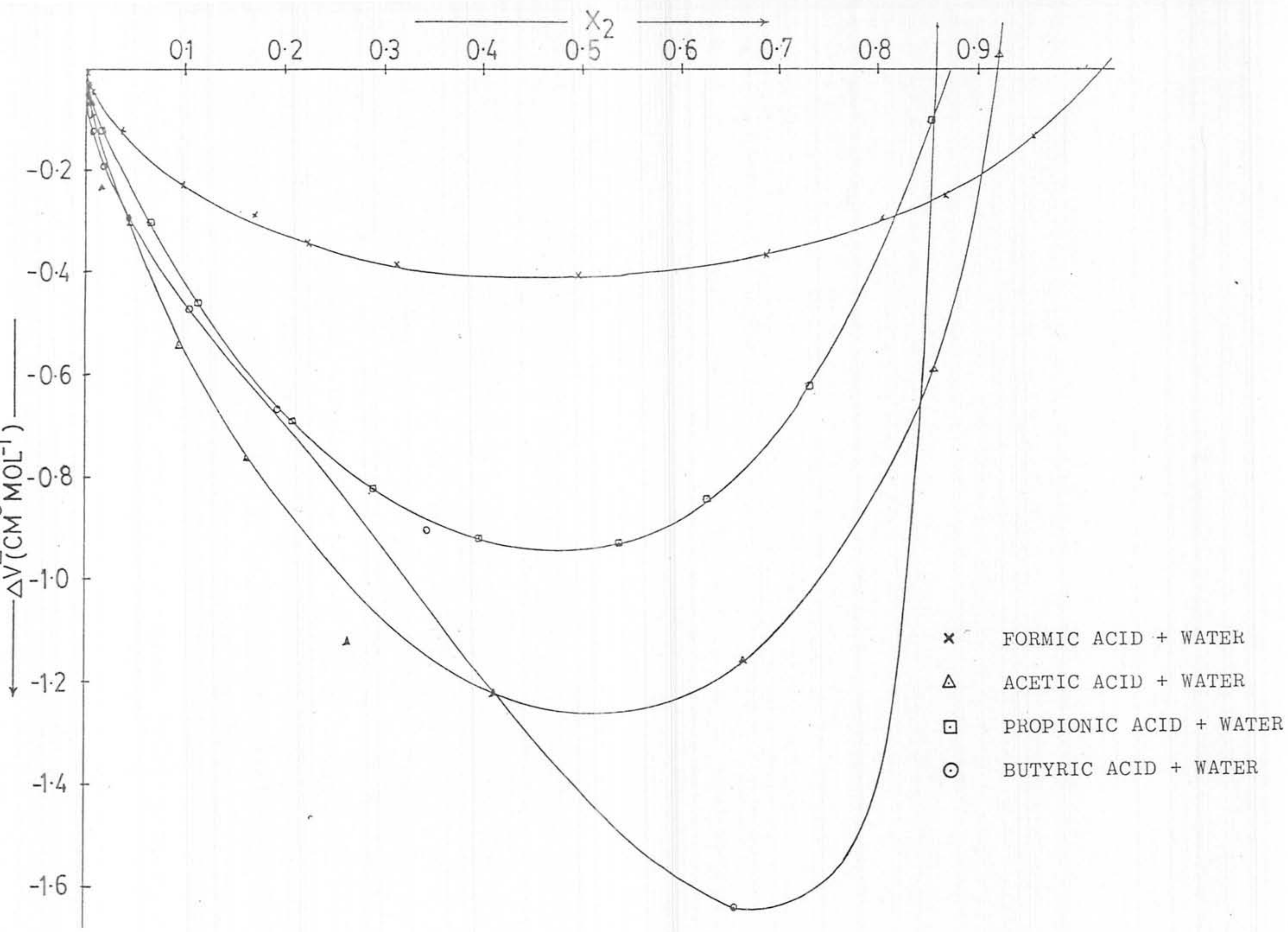


FIGURE 23. PLOT OF EXCESS VOLUME (ΔV^E) VS. MOLE FRACTION (X_2) OF ACID AT 45°C.

TABLE - 6.

Excess Viscosity (η^E) and Excess Volume (ΔV^E) of Binary Liquid Mixture at 50°C...

S. No.	Mol. Frac.of Formic Acid-X_2	Formic Acid+ Water System		Mol. Frac.of Acetic Acid.X_2	Acetic Acid+ Water System		Mol. Frac.of Propanoic Acid.X_2	Propionic Acid+ Water System		Mol. Frac.of Butyric Acid.X_2	Butyric Acid+ Water System	
		η^E (cp)	ΔV^E (cm^{3}mol^{-1})		η^E (cp)	ΔV^E (cm^{3}mol^{-1})		η^E (cp)	ΔV^E (cm^{3}mol^{-1})		η^E (cp)	ΔV^E cm^3 mol^{-1})
1.	0.002	0.006	-0.051	0.002	0.004	-0.043	0.002	0.011	-0.067	0.002	0.019	-0.022
2.	0.009	0.012	-0.047	0.009	0.025	-0.084	0.009	0.039	-0.115	0.009	0.052	-0.122
3.	0.018	0.014	-0.078	0.019	0.051	-0.174	0.019	0.082	-0.232	0.019	0.099	-0.192
4.	0.038	0.024	-0.122	0.064	0.129	-0.309	0.041	0.162	-0.303	0.042	0.226	-0.298
5.	0.099	0.039	-0.216	0.111	0.213	-0.452	0.093	0.336	-0.543	0.102	0.541	-0.479
6.	0.170	0.058	-0.286	0.207	0.350	-0.679	0.163	0.511	-0.770	0.192	0.773	-0.689
7.	0.223	0.067	-0.361	0.289	0.443	-0.819	0.261	0.661	-0.997	0.345	0.890	-0.909
8.	0.312	0.082	-0.381	0.396	0.498	-0.906	0.409	0.736	-1.205	0.660	0.780	-1.649
9.	0.495	0.098	-0.526	0.535	0.514	-0.926	0.657	0.569	-1.084	0.861	0.060	+0.157
10.	0.686	0.127	-0.383	0.624	0.455	-0.836	0.858	0.219	-0.577	–	–	–
11.	0.080	0.077	-0.311	0.729	0.332	-0.604	0.916	0.015	+0.039	–	–	–
12.	0.865	0.045	-0.265	0.849	0.059	-0.998	–	–	–	–	–	–
13.	0.951	0.020	-0.153	–	–	–	–	–	–	–	–	–

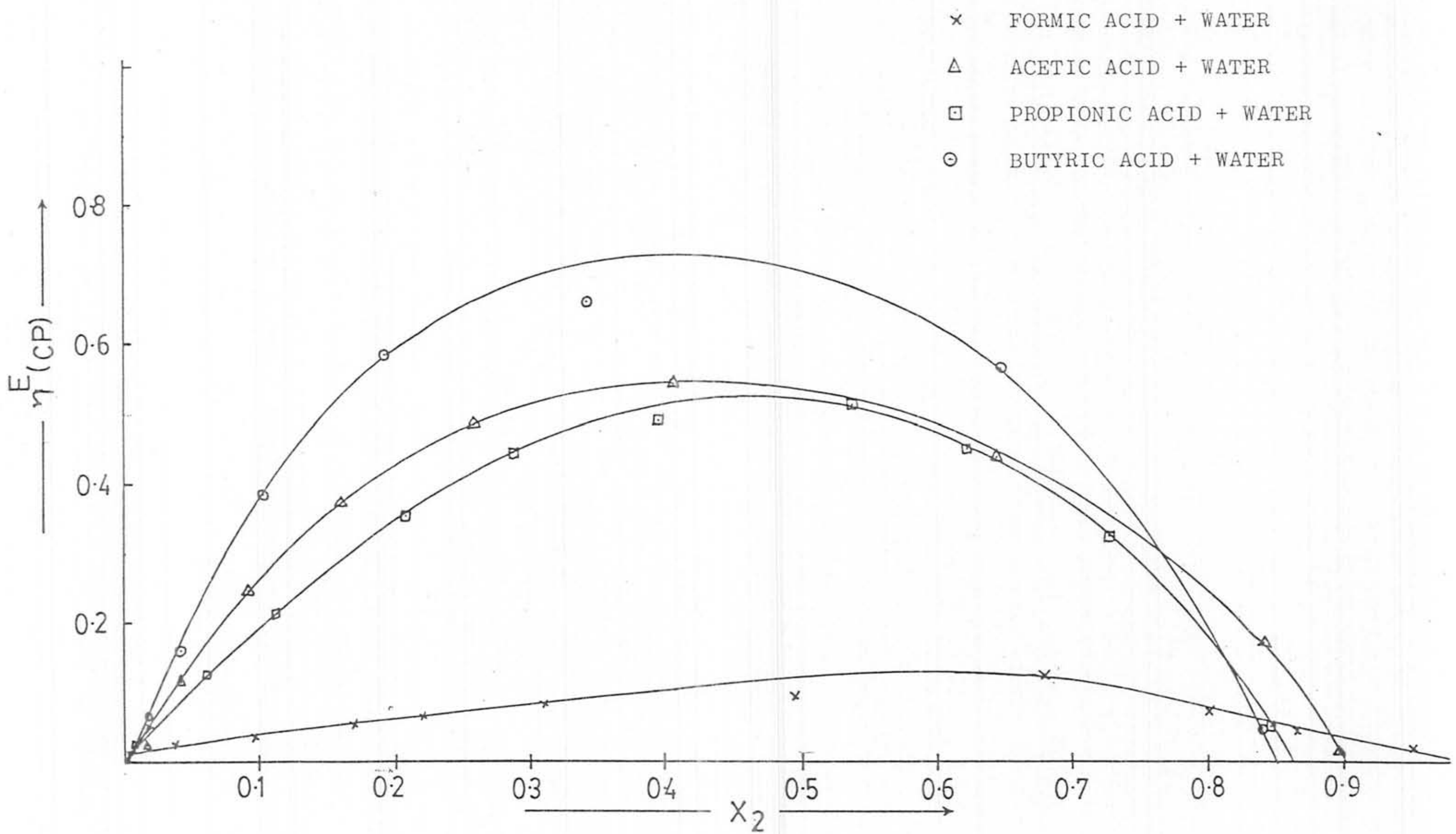


FIGURE 16. PLOT OF EXCESS VISCOSITY (η^E) VS. MOLE FRACTION OF ACID AT 50°C.

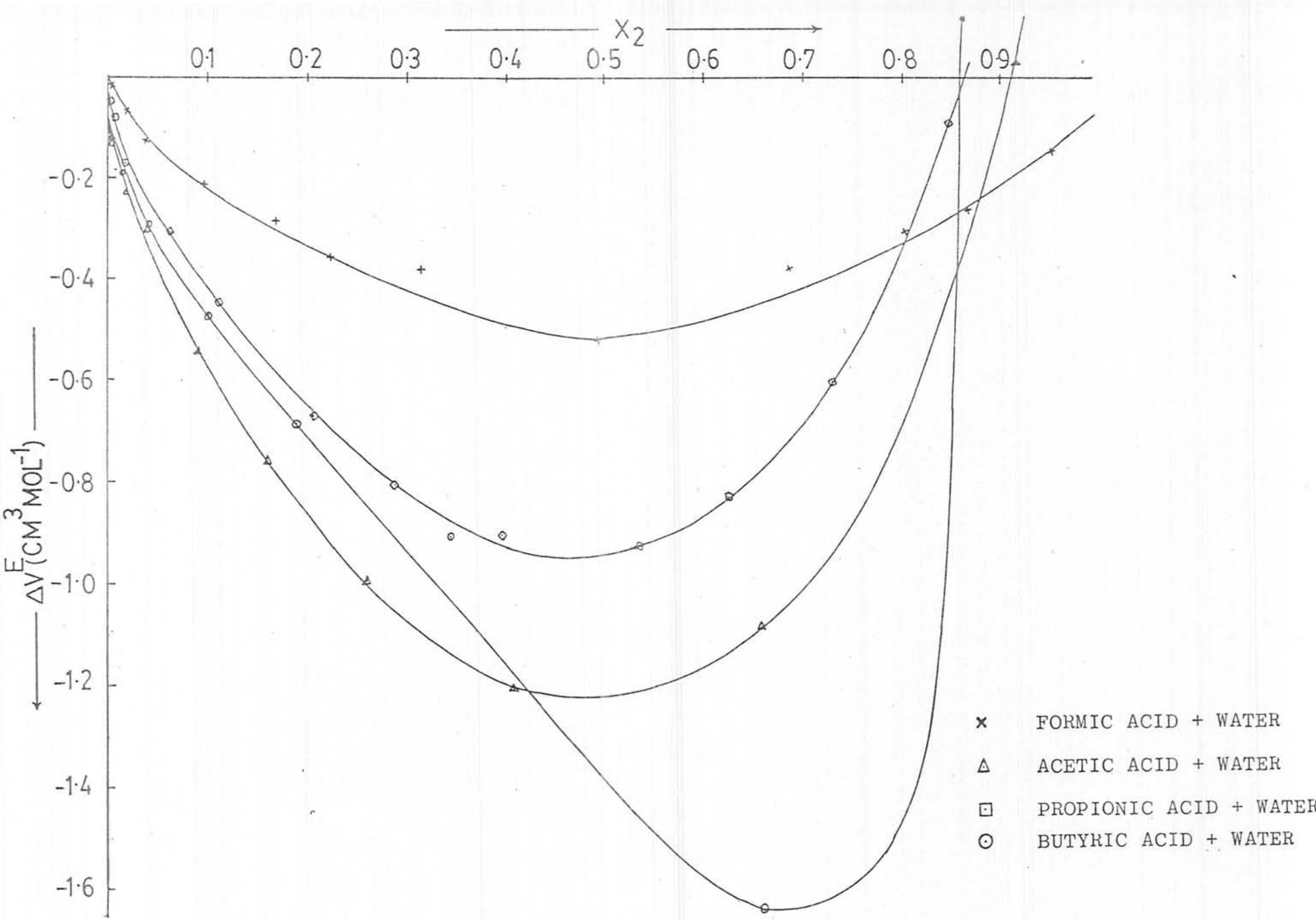


FIGURE 24. PLOT OF EXCESS VOLUME (ΔV^E) VS. MOLE FRACTION (X_2) OF ACID AT 50°C.

TABLE - 7.

Excess Viscosity (η^E) and Excess Volume (ΔV^E) of Binary Liquid Mixture at 55°C.

S. No.	Mol. Frac.of Formic Acid-X_2	Formic Acid+ Water System		Mol. Frac.of Acetic Acid.X_2	Acetic Acid+ Water System		Mol. Frac.of Propanoic Acid.X_2	Propionic Acid+ Water System		Mol. Frac.of Butyric Acid.X_2	Butyric Acid+ Water System	
		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$
1.	0.002	0.002	-0.041	0.002	0.002	-0.055	0.002	0.007	-0.062	0.002	0.014	-0.051
2.	0.009	0.007	-0.039	0.009	0.018	-0.089	0.009	0.030	-0.112	0.009	0.042	-0.115
3.	0.018	0.011	-0.080	0.019	0.032	-0.124	0.019	0.067	-0.232	0.194	0.084	-0.194
4.	0.038	0.019	-0.119	0.061	0.107	-0.302	0.041	0.138	-0.312	0.042	0.191	-0.319
5.	0.099	0.033	-0.207	0.111	0.183	-0.455	0.093	0.286	-0.546	0.101	0.459	-0.489
6.	0.170	0.051	-0.273	0.206	0.309	-0.683	0.162	0.434	-0.768	0.191	0.685	-0.686
7.	0.223	0.064	-0.344	0.289	0.381	-0.824	0.260	0.572	-0.998	0.343	0.821	-0.924
8.	0.311	0.076	-0.378	0.394	0.441	-0.891	0.407	0.633	-1.196	0.655	0.669	-1.633
9.	0.494	0.092	-0.392	0.533	0.447	-0.921	0.653	0.499	-1.168	0.852	0.062	+0.172
10.	0.683	0.103	-0.393	0.621	0.411	-0.841	0.851	0.166	-0.549	-	-	-
11.	0.798	0.073	-0.310	0.725	0.289	-0.611	0.908	0.016	+0.048	-	-	-
12.	0.861	0.057	-0.287	0.843	0.055	-0.096	-	-	-	-	-	-
13.	0.947	0.021	-0.155	-	-	-	-	-	-	-	-	-

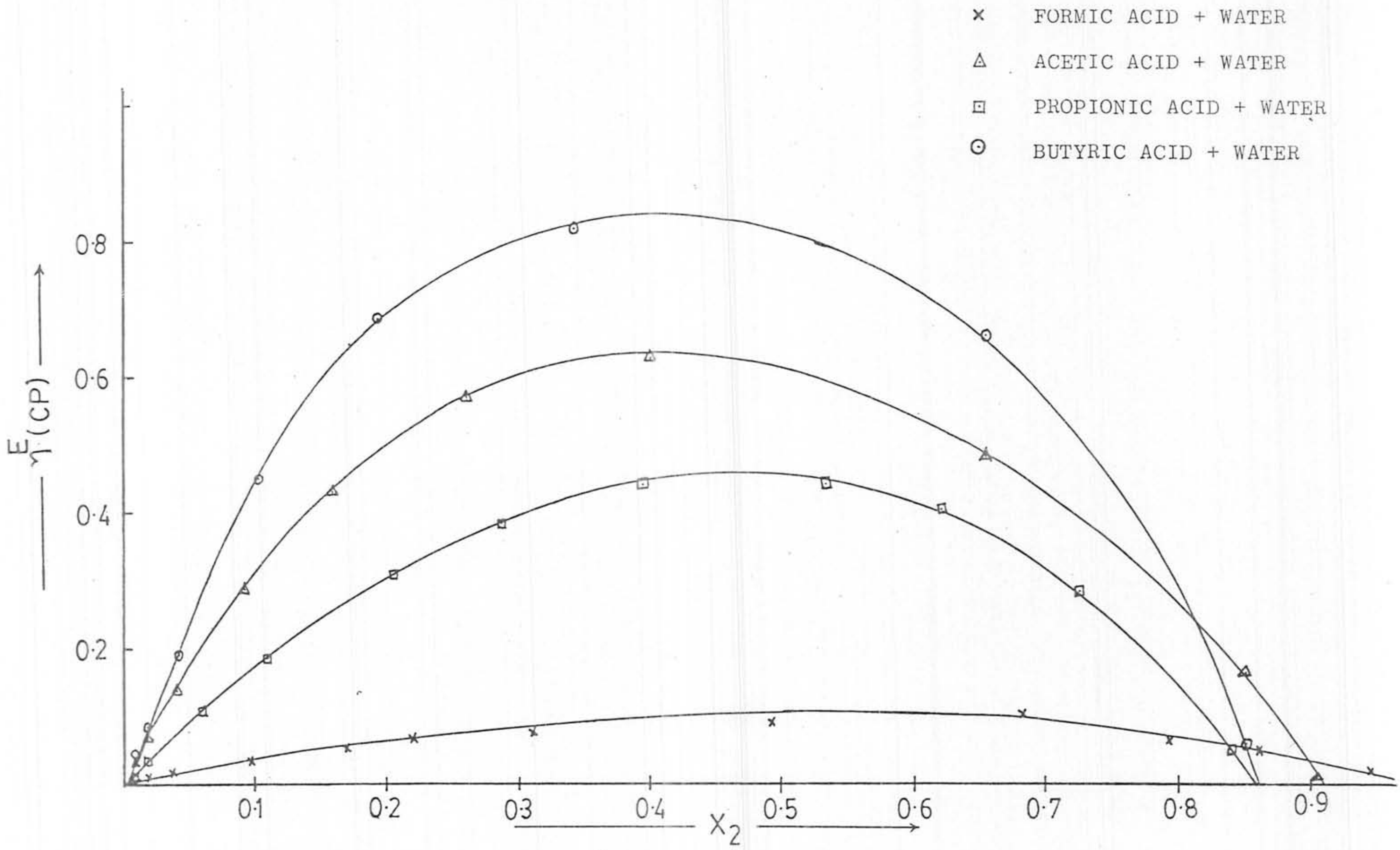


FIGURE 17. PLOT OF EXCESS VISCOSITY (η^E) VS. MOLE FRACTION OF ACID AT 55°C.

TABLE - 8.

Excess Viscosity (η^E) and Excess Volume ΔV^E of Binary Liquid Mixture at 60°C.

S. No.	Mol. Frac.of Formic Acid-X_2	Formic Acid+ Water System		Mol. Frac.of Acetic Acid.X_2	Acetic Acid+ Water System		Mol. Frac.of Propanoic Acid.X_2	Propanoic Acid+ Water System		Mol. Frac.of Butyric Acid.X_2	Butyric Acid+ Water System	
		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)
1.	0.002	0.002	-0.053	0.002	0.001	-0.053				0.002	0.011	-0.041
2.	0.009	0.007	-0.063	0.009	0.012	-0.093	0.009	0.026	-0.113	0.009	0.035	-0.119
3.	0.018	0.009	-0.067	0.019	0.020	-0.122	0.019	0.057	-0.192	0.019	0.062	-0.199
4.	0.037	0.015	-0.125	0.061	0.095	-0.311	0.041	0.117	-0.311	0.042	0.161	-0.298
5.	0.099	0.029	-0.201	0.111	0.158	-0.451	0.093	0.245	-0.541	0.101	0.389	-0.483
6.	0.170	0.045	-0.277	0.206	0.266	-0.682	0.162	0.376	-0.765	0.191	0.586	-0.685
7.	0.222	0.055	-0.326	0.288	0.333	-0.822	0.259	0.489	-0.999	0.342	0.662	-0.906
8.	0.311	0.069	-0.376	0.393	0.381	-0.905	0.405	0.549	-1.194	0.649	0.572	-1.649
9.	0.493	0.083	-0.388	0.531	0.385	-0.910	0.649	0.441	-1.172	0.842	0.058	+0.196
10.	0.681	0.093	-0.389	0.618	0.422	-0.840	0.843	0.178	-0.613	-	-	-
11.	0.794	0.062	-0.308	0.721	0.248	-0.618	0.899	0.016	+0.058	-	-	-
12.	0.858	0.045	-0.266	0.838	0.052	-0.089	-	-	-	-	-	-
13.	0.942	0.021	-0.171	-	-	-	-	-	-	-	-	-

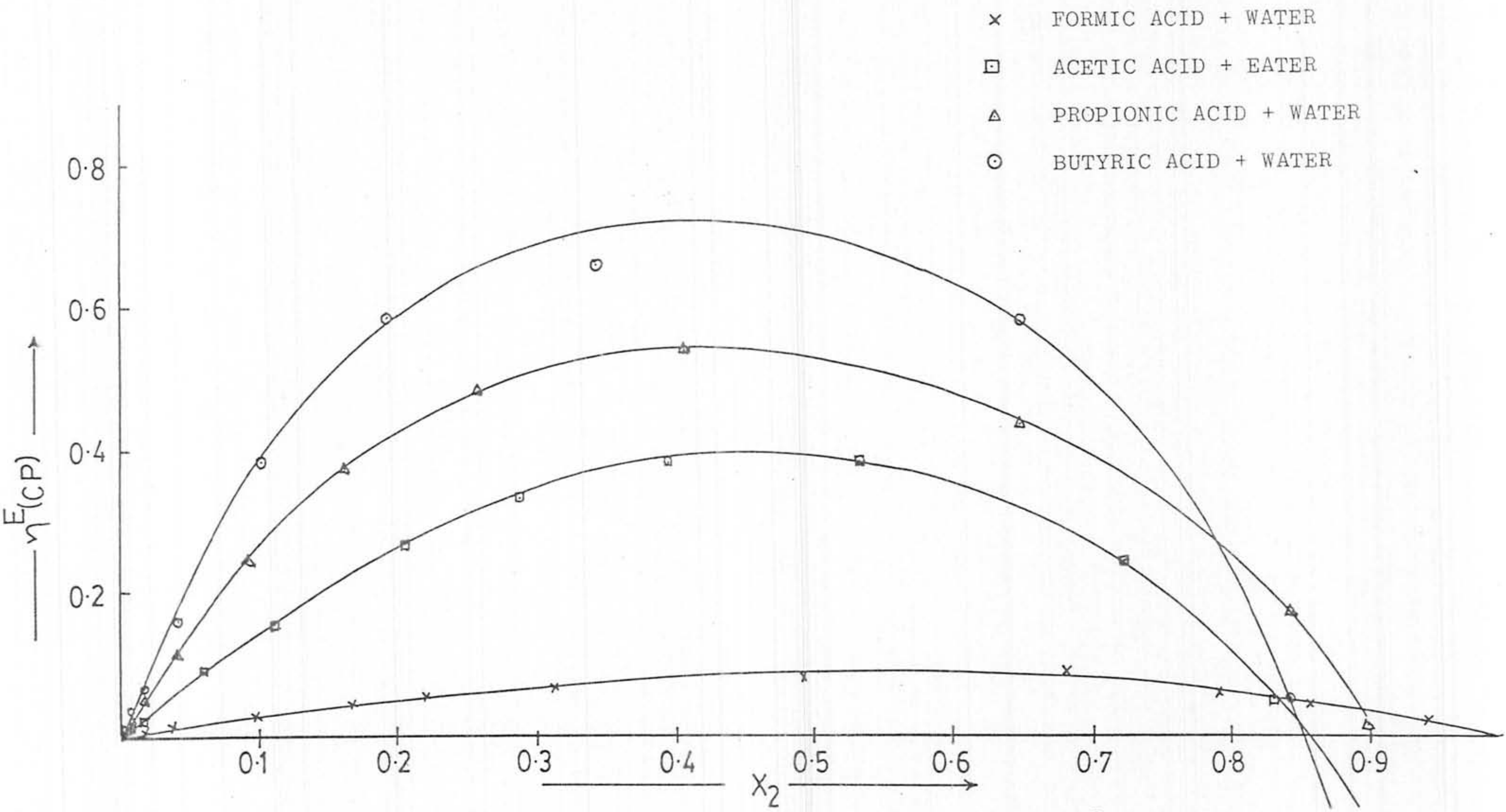


FIGURE 18. PLOT OF EXCESS VISCOSITY (η^E) VS. MOLE FRACTION OF ACID AT 60°C.

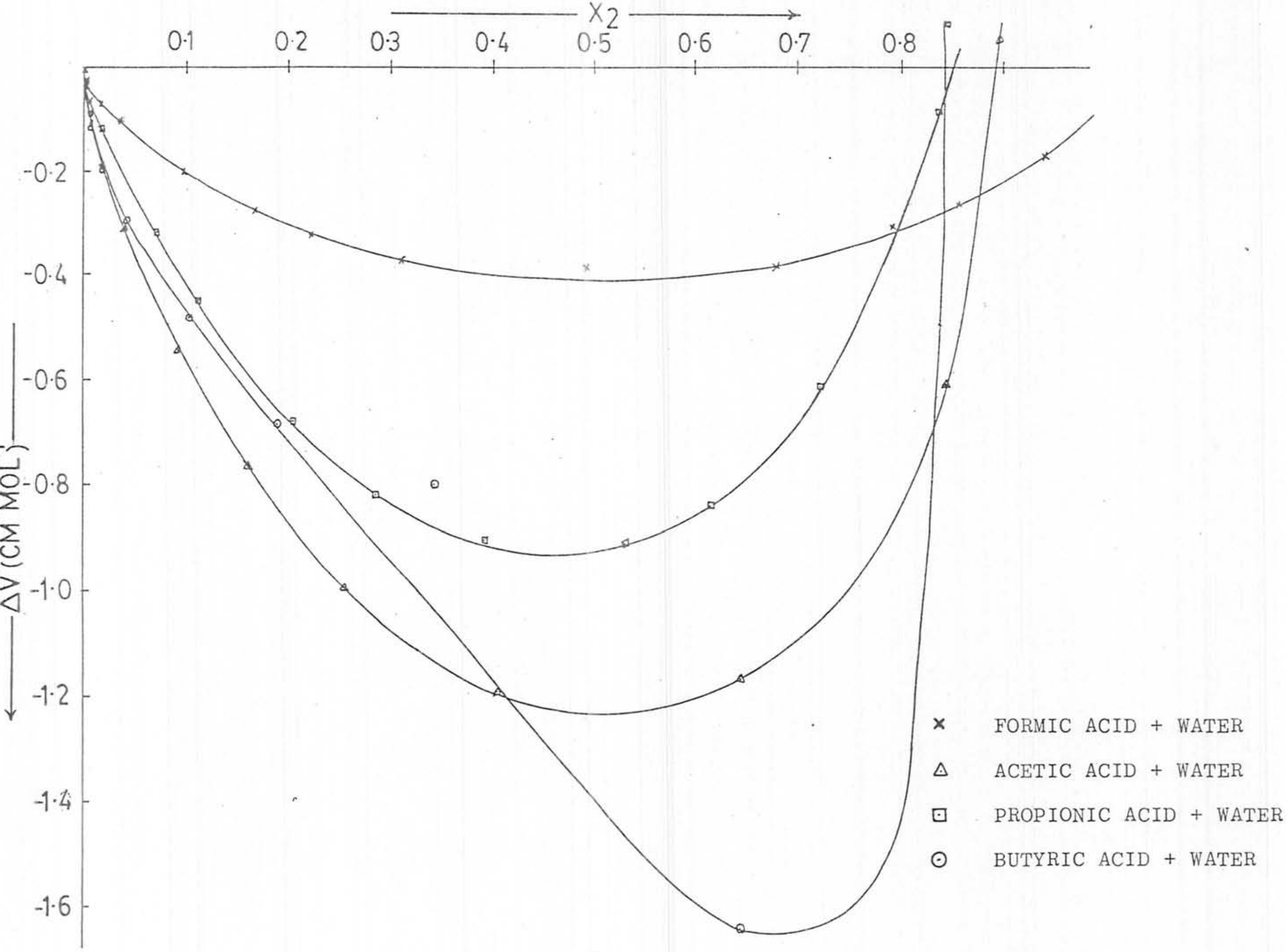


FIGURE 25. PLOT OF EXCESS VOLUME (ΔV^E) VS. MOLE FRACTION (X_2) OF ACID AT 60°C.

TABLE - 9.

Excess Viscosity (η^E) and Excess Volume (ΔV^E) of Binary Liquid Mixture at 65°C.

S. No.	Mol. Frac.of Formic Acid-X_2	Formic Acid+ Water System		Mol. Frac.of Acetic Acid.X_2	Acetic Acid+ Water System		Mol. Frac.of Propanoic Acid.X_2	Propionic Acid+ Water System		Mol. Frac.of Butyric Acid.X_2	Butyric Acid+ Water System	
		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)		η^E (cp)	ΔV^E ($cm^3 mol^{-1}$)
1.	0.002	0.002	-0.039	0.002	0.002	-0.051	0.002	-0.004	-0.066	0.002	0.009	-0.006
2.	0.009	0.008	-0.067	0.009	0.014	-0.093	0.009	0.023	-0.112	0.009	0.032	-0.120
3.	0.018	0.009	-0.073	0.019	0.026	-0.132	0.019	0.050	-0.238	0.019	0.065	-0.117
4.	0.037	0.015	-0.109	0.061	0.082	-0.298	0.041		-0.308	0.042	0.141	-0.296
5.	0.099	0.031	-0.204				0.093	0.213	-0.536	0.101	0.339	-0.82
6.	0.169	0.048	-0.280	0.206	0.227	-0.671	0.162	0.328	-0.771	0.190	0.407	-0.523
7.	0.222	0.060	-0.331	0.288	0.298	-0.819	0.259	0.429	-0.989	0.340	0.577	-0.902
8.	0.310	0.076	-0.373	0.392	0.329	-0.906	0.404	0.481	-1.197	0.644	0.495	-1.635
9.	0.491	0.095	-0.397	0.529	0.336	-0.931	0.644	0.383	-1.172	0.833	0.057	+0.218
10.	0.678	0.102	-0.406	0.614	0.312	-0.867	0.825	0.153	-0.572	-	-	-
11.	0.791	0.081	-0.343	0.716	0.227	-0.613	0.890	0.018	+0.070	-	-	-
12.	0.853	0.069	-0.292	0.832	0.049	+0.085	-	-	-	-	-	-
13.	0.937	0.019	-0.183	-	-	-	-	-	-	-	-	-

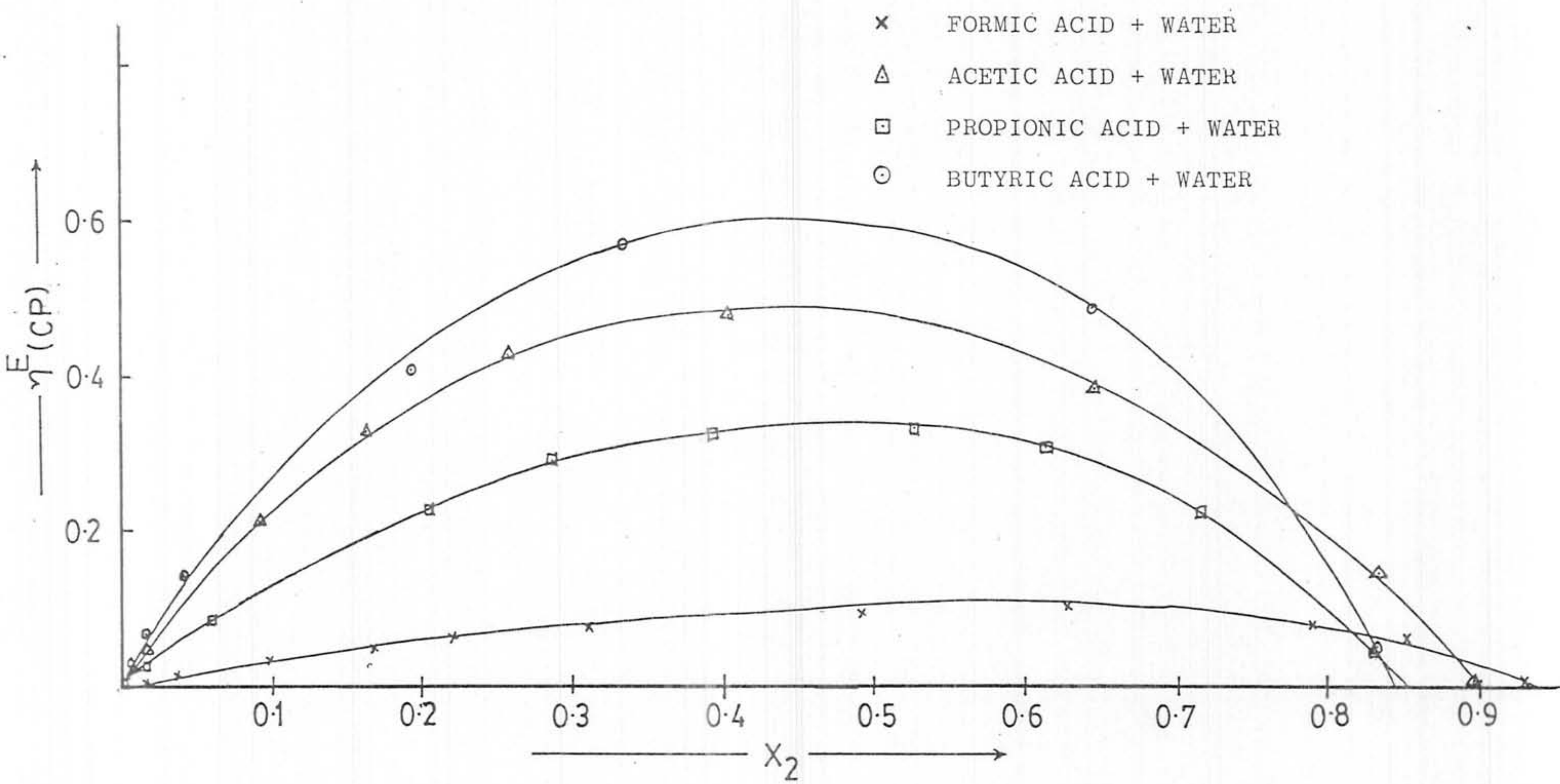


FIGURE 19. PLOT OF EXCESS VISCOSITY (η^E) VS. MOLE FRACTION OF ACID, AT 65°C.

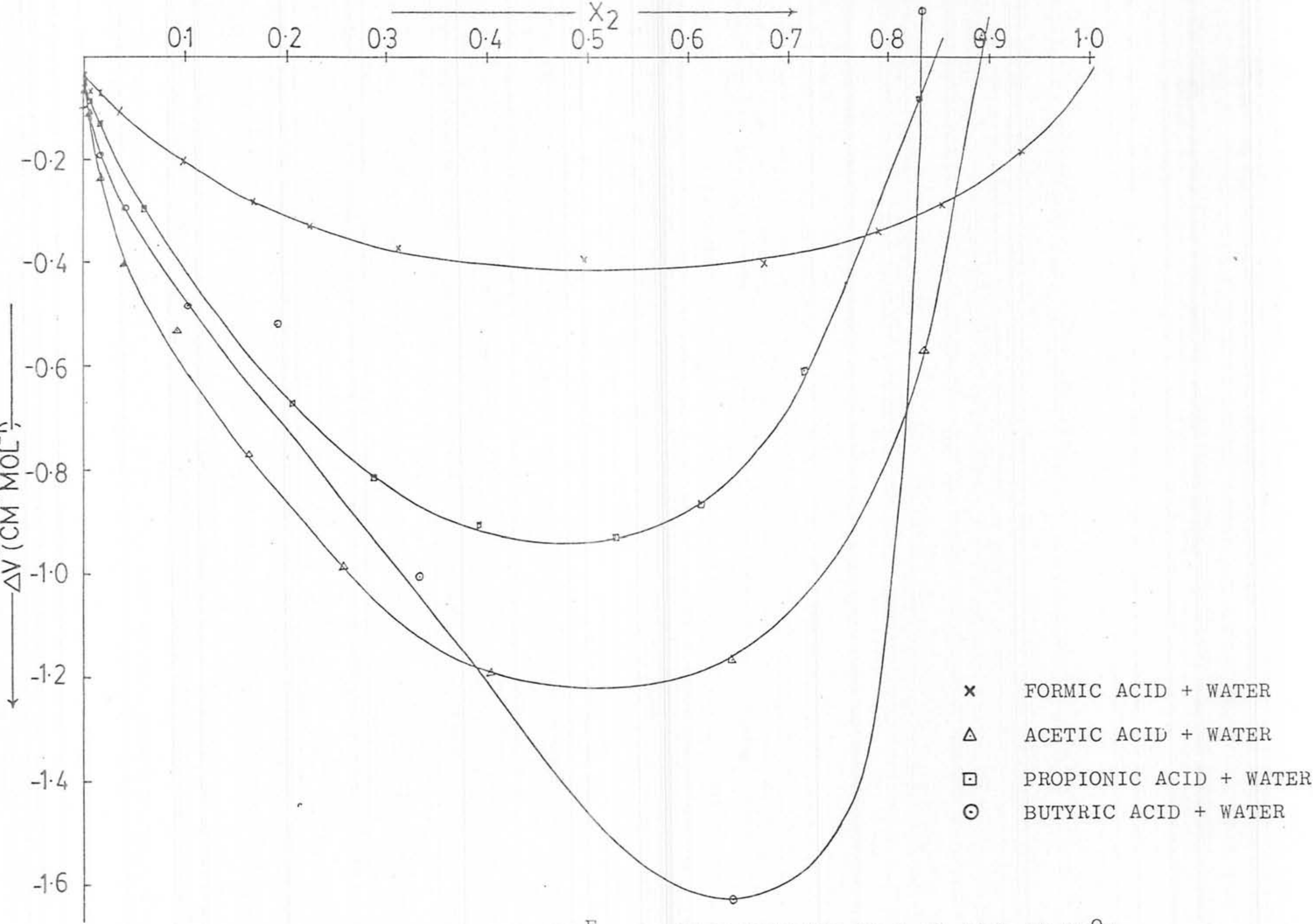


FIGURE 26. PLOT OF EXCESS VOLUME (ΔV^E) VS. MOLE FRACTION (X_2) OF ACID AT 65°C.

TABLE - 10.

1. Conc. of Formic Acid = 0.1 M.
2. Conc. of Acetic Acid = 0.1 M.
3. Conc. of Propionic Acid = 0.1 M.
4. Conc. of Butyric Acid = 0.1 M.

S.No.	Temp.	Formic Acid+Water Sys.		Acetic Acid+Water Sys.		Propionic Acid+Water Sys.		Butyric Acid+Water Sys.	
		Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$
1.	25°C	18.085	24.430	18.103	24.429	18.199	24.449	-	-
2.	32°C	18.131	24.280	18.138	24.276	18.156	24.289	18.196	24.313
3.	37°C	18.163	24.185	18.168	24.178	18.181	24.193	18.211	24.219
4.	40°C	18.181	24.124	18.192	24.122	18.199	24.133	18.234	24.157
5.	45°C	18.237	24.035	18.224	24.051	18.232	24.046	18.283	24.066
6.	50°C	18.218	23.954	18.266	23.953	18.272	23.965	18.349	23.984
7.	55°C	18.271	23.868	18.294	23.868	18.321	23.879	18.364	23.896
8.	60°C	18.306	23.792	18.343	23.792	18.759	-	18.421	23.818
9.	65°C	18.369	23.723	18.395	23.724	18.414	23.711	18.507	23.746

Calculated Values of $\ln\frac{\eta V}{hN}$ of the Aqueous Mixture of Carboxylic Acid at Various Mole Fraction.

TABLE - 11.

1. Conc. of Formic Acid = 1 M.
2. Conc. of Acetic Acid = 1 M.
3. Conc. of Propionic Acid = 2 M.
4. Conc. of Butyric Acid = 2 M.

S.No.	Temp.	Formic Acid+Water Sys.		Acetic Acid+Water Sys.		Propionic Acid+Water Sys.		Butyric Acid+Water Sys	
		Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$
1.	25°C	18.353	24.472	18.661	24.531	20.053	24.874	20.874	25.034
2.	32°C	18.402	24.320	18.687	24.397	20.116	24.696	20.930	24.855
3.	37°C	18.426	24.232	18.749	24.302	20.167	24.589	20.999	24.740
4.	40°C	18.449	24.170	18.781	24.236	20.199	24.521	21.039	24.663
5.	45°C	18.495	24.079	18.829	24.145	20.949	24.415	21.098	24.561
6.	50°C	18.534	23.998	18.869	24.061	20.309	24.319	21.158	24.460
7.	55°C	18.577	23.915	18.885	23.970	20.358	24.224	21.199	24.356
8.	60°C	18.639	23.838	18.966	23.877	20.423	24.131	21.283	24.258
9.	65°C	18.687	23.768	19.009	23.822	20.487	24.047	21.359	24.173

Calculated Values of $\ln\frac{\eta V}{hN}$ of the Aqueous Mixture of Carboxylic Acid at Various Mole Fraction.

TABLE - 12.

1. Conc. of Formic Acid = 5 M.
2. Conc. of Acetic Acid = 5 M.
3. Conc. of Propionic Acid = 6 M.
4. Conc. of Butyric Acid = 4 M.

S.No.	Temp.	Formic Acid+Water Sys.		Acetic Acid+Water Sys.		Propionic Acid+Water Sys.		Butyric Acid+Water Sys.	
		Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln\frac{\eta V}{hN}$
1.	25°C	19.799	24.641	21.912	25.073	26.548	25.629	25.139	25.636
2.	32°C	19.849	24.485	22.011	24.901	26.669	25.439	25.237	25.438
3.	37°C	19.919	24.405	22.072	24.792	26.758	25.322	25.316	25.314
4.	40°C	19.247	24.344	22.114	24.724	26.815	25.241	25.367	25.233
5.	45°C	20.003	24.259	22.189	24.619	26.916	25.127	25.446	25.112
6.	50°C	20.073	24.181	22.260	24.525	27.001	25.021	25.523	25.006
7.	55°C	20.139	24.094	22.327	24.428	27.094	24.907	25.593	24.888
8.	60°C	20.205	24.018	22.327	24.336	27.193	24.804	26.682	24.775
9.	65°C	20.268	23.949	-	-	27.282	24.709	25.768	24.677

Calculated Values of $\ln\frac{\eta V}{hN}$ of the Aqueous Mixture of Carboxylic Acid at Various Mole Fraction.

TABLE - 13.

1. Conc. of Formic Acid = 13 M.
2. Conc. of Acetic Acid = 8 M.
3. Conc. of Propionic Acid = 8 M.
4. Conc. of Butyric Acid = 6 M.

S.No.	Temp.	Formic Acid+Water Sys.		Acetic Acid+Water Sys.		Propionic Acid+Water Sys.		Butyric Acid+Water Sys
		Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$
1.	25°C	23.855	24.999	25.440	25.442	31.984	25.959	31.711	26.100
2.	32°C	23.969	24.862	25.559	25.262	32.133	25.775	31.854	25.904
3.	37°C	24.051	24.783	25.644	25.152	32.248	25.653	31.947	25.776
4.	40°C	24.114	24.786	25.785	25.081	32.234	25.573	32.011	25.691
5.	45°C	24.201	24.641	25.785	24.970	32.296	25.454	32.107	25.571
6.	50°C	24.288	24.567	25.886	24.873	32.528	25.350	32.205	25.452
7.	55°C	24.374	24.484	25.969	24.778	32.633	25.241	32.305	25.352
8.	60°C	24.457	24.409	26.058	24.678	32.714	25.129	32.404	25.237
9.	65°C	24.552	24.343	26.162	24.580	32.855	25.032	32.664	25.134

Calculated Values of $\ln \frac{\eta V}{hN}$ of the Aqueous Mixture of Carboxylic Acid at Various Mole Fraction.

TABLE - 14.

1. Conc. of Formic Acid = 18 M.
2. Conc. of Acetic Acid = 10 M.
3. Conc. of Propionic Acid = 10 M.
4. Conc. of Butyric Acid = 8 M.

S.No.	Temp.	Formic Acid+Water Sys.		Acetic Acid+Water Sys.		Propionic Acid+Water Sys.		Butyric Acid+Water Sys.	
		Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$
1.	25°C	27.555	25.263	28.607	25.681	40.396	26.259	43.099	26.514
2.	32°C	27.687	25.132	28.737	25.499	40.569	26.079	43.273	26.326
3.	37°C	27.798	25.048	28.839	25.385	40.697	25.973	42.390	26.205
4.	40°C	27.849	24.991	28.889	25.314	40.805	25.885	43.448	26.122
5.	45°C	27.953	24.877	28.979	25.207	42.878	25.776	43.558	25.998
6.	50°C	27.925	24.826	29.093	25.110	40.993	25.662	43.669	25.879
7.	55°C	28.156	24.745	29.186	25.003	41.108	25.546	43.744	25.799
8.	60°C	28.156	24.671	29.186	24.905	41.216	25.439	43.849	25.648
9.	65°C	28.349	24.606	29.390	24.819	41.311	25.342	43.936	25.543

Calculated Values of $\ln \frac{\eta V}{hN}$ of the Aqueous Mixture of Carboxylic Acid at Various Mole Fraction.

TABLE - 15.

1. Conc. of Formic Acid = 24 M.
2. Conc. of Acetic Acid = 12 M.
3. Conc. of Propionic Acid = 12 M.
4. Conc. of Butyric Acid = 9 M.

S.No.	Temp.	Formic Acid+Water Sys.		Acetic Acid+Water Sys.		Propionic Acid+Water Sys.		Butyric Acid+Water Sys.	
		Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$
1.	25°C	33.894	25.608	32.719	25.918	-	-	67.035	26.954
2.	32°C	34.054	25.470	32.890	25.731	55.304	26.249	67.116	26.766
3.	37°C	34.186	25.382	32.997	25.620	55.387	26.145	67.139	26.647
4.	40°C	34.246	25.322	33.063	25.552	55.582	26.078	67.143	26.567
5.	45°C	34.358	25.238	33.136	25.436	55.550	25.970	67.116	26.639
6.	50°C	34.451	25.161	33.282	25.328	55.598	25.873	57.068	26.325
7.	55°C	34.556	25.072	33.400	25.231	55.651	25.770	67.028	26.206
8.	60°C	34.650	24.993	33.489	25.126	55.689	25.672	66.929	26.089
9.	65°C	34.779	24.918	33.594	25.027	55.714	25.578	66.845	25.982

Calculated Values of $\ln \frac{\eta V}{hN}$ of the Aqueous Mixture of Carboxylic Acid at Various Mole Fraction.

TABLE - 16.

1. Conc. of Formic Acid = 26.95 M.
2. Conc. of Acetic Acid = 16.95 M.
3. Conc. of Propionic Acid = 13.23 M.
4. Conc. of Butyric Acid = 10.68 M.

S.No.	Temp.	Formic Acid+Water Sys.		Acetic Acid+Water Sys.		Propionic Acid+Water Sys.		Butyric Acid+Water Sys.	
		Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$	Mol. Vol. of Mix.(V)	$\ln \frac{\eta V}{hN}$
1.	25°C	37.178	25.712	51.876	25.978	71.903	25.937	84.687	26.477
2.	32°C	37.351	25.587	52.052	25.846	72.023	25.836	84.690	26.350
3.	37°C	37.466	25.494	52.176	25.767	72.075	25.877	84.631	26.273
4.	40°C	37.533	25.431	52.215	25.701	72.082	25.727	84.590	26.215
5.	45°C	37.628	25.342	52.313	25.611	70.052	25.659	84.408	26.135
6.	50°C	37.750	25.263	52.369	25.533	71.992	25.596	84.208	26.053
7.	55°C	37.813	25.170	52.431	25.446	71.920	25.525	83.984	25.966
8.	60°C	37.883	25.098	52.479	26.362	71.831	25.454	83.717	25.886
9.	65°C	37.979	24.988	52.523	25.288	71.709	25.393	83.435	25.808

Calculated Values of $\ln \frac{\eta V}{hN}$ of the Aqueous Mixture of Carboxylic Acid at Various Mole Fraction.

TABLE - 17.

ACTIVATION PARAMETER FOR VISCOUS FLOW

System	Concentration (M)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	System	Concentration (M)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
Formic Acid & Water	0.1	1406.98	-1.330	2199.80	Propionic Acid & Water.	0.1	1452.02	-1.397	1868.25
	1	1454.95	-0.882	1717.57		2	1726.75	-1.538	2185.10
	5	1454.95	-1.060	2086.73		6	1900.34	-2.087	2522.21
	13	1385.67	-0.998	1682.98		8	193.93	-2.045	2549.41
	24	1432.57	-1.247	1804.21		10	1884.50	-1.879	2444.43
	26.95	1478.04	-0.657	1673.77		12	1745.94	-1.280	2127.49
	-	-	-	-		13.23	1163.96	-0.208	1225.89
Acetic Acid & Water.	0.1	1425.26	-1.289	1809.28	Butyric Acid & Water	0.1	1454.95	-1.123	1789.42
	1	1496.52	-1.347	1897.89		2	1790.71	-1.454	2224.29
	5	1662.80	-2.411	2381.29		4	1965.13	-1.746	2485.42
	8	1721.35	-1.372	2139.14		6	1995.36	-2.087	2617.23
	10	1760.61	-1.813	2300.72		8	2054.05	-2.079	2673.44
	12	1861.86	-1.954	2444.09		9	2032.13	-1.704	2540.21
	15	1810.37	-1.829	2373.83		10.68	1385.67	-1.289	1769.69
	16.95	1451.17	-0.723	1666.65		-	-	-	-

Units $\Delta H^{\ddagger}$, $\Delta G^{\ddagger} \Delta S^{\ddagger}$ (J mol^{-1}).

CHAPTER - 5

DISCUSSION

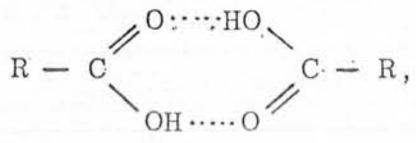
The present investigation was undertaken to study the nature of association of simple bifunctional organic molecules in aqueous solution. We are reporting results for formic, acetic, propionic and butyric acids in water at various concentrations. The particular aspect under which the association of these molecules is of interest is the hydrophobic interaction. This denotation implies that in aqueous solution of organic molecules with (inert) alkyl groups besides other forces, there should be an attractive force

$$K = \frac{\partial F^{22}(r_{22})}{\partial r_{22}}$$

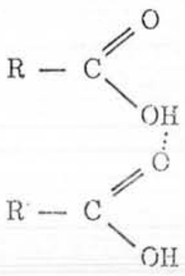
acting between the solute molecules which tends to bring the hydrophobic parts in more or less contact. $F^{22}(r_{22})$ is the partial free energy of a pair of solute molecules under the condition that the distance between the two molecules is r_{22} (solute = species 2, the solvent water is denoted as species 1) The important point is the dominant contribution to the force K is ascribed to entropy factor, that is $\partial S^{22}(r_{22})/\partial r_{22} < 0$. Thus when the two hydrophobic parts of the molecules come in contact, the two hydration sphere surrounding these groups (hydrophobic hydration) coalesce which gives an increase of entropy per solute molecule.[137]

Now if such an attractive force acts, the probability of finding a second solute molecule in close vicinity of a solute molecule selected at random should be greater than in the case when the hydrophobic force is absent and only the hydrogen bonds are effective to couple the two solute molecules to one another.

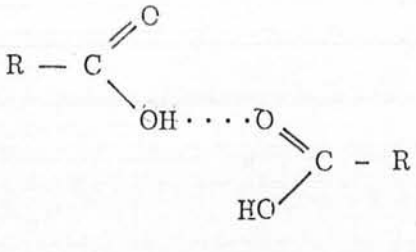
For various qualitative reasons the dimers were expected to be of one of the extended forms II or III not of the cyclic form I.[60,138]



I



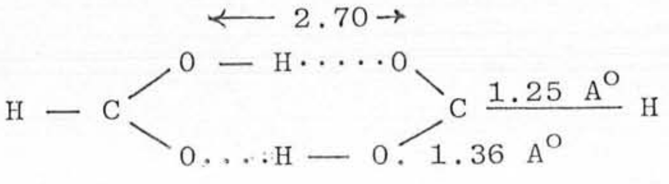
II



III

However, the decision between the pair configurations (II) or (III) is still open. For butyric acid K_D was found to be in the range $0.1 < K_D < 0.5$ M^{-1}, depending somewhat on the method applied, K_D for formic acid is roughly one order of magnitude smaller, association of the other acids ranges more or less between these limits[138]. Thus the longer the hydrocarbon chain the stronger is the association of the acid of course, this gives support to the hypothesis of hydrophobic association. As a consequence, pair configuration (II) was proposed by Schrier et. al.[138]. According to Martin and Rossotli[60] the configuration III should be the correct one. The increase of the strength of association has to be ascribed to configurational effects.

All the viscosities and densities were determined as described in Chapter,4 by using the formulas 1,2, by plotting viscosity vs concentration at various temperatures as shown in Figures 1-4. The viscosity increase with increase in concentration may be explaine by hydrogen bonding in acid-water system. The hydrogen bonds formed by water are not sufficiently strong to lead to an appreciable concentration of the polymerized molecule in the vapour phase. The oxygen atom of carboxylic group can however, form stronger hydrogen bonds leading to the formation of stable double molecules of formic acid, and acetic acid. The structure of the formic acid dimer as determined by electron difraction[37] is given



The vaoues 2.70 A° for O - H ... O distance in this substance is smaller than that in ice 2.76 A° as expected for this stronger bond.

The distance from each hydrogen atom to the nearer of the two adjacent oxygen atoms in the acetic acid has been reported to be 1.075 ± 0.05 A^{o}. This is considerabily greater than the value 1.01 A^{o}, as is to be expected in consequence of the increase strength of the hydrogen bond.

From the enthalpy of dimerization 14.12 Kcal/mol, the $\overset{\longleftarrow 2.70 \rightarrow}{0 - H \ldots 0}$ bond energy is found to have the value 7.06 Kcal/mole. The value 7.6 Kcal/mol is similar found for the hydrogen bond energy in acetic acid[38,139]. These values are 50 percent greater than these of ice. The strength of the hydrogen bond in these acids seem to increase from formic to butyric acid which increases, until it reaches a maximum at 26.95 M, 14 M, 10 M, and 8.5 M of formic, acetic, propionic and butyric acids respectively. The presence of a viscosity maximum[140] as a function of concentration is in agreement with the Frank-Ives[141] conclusion. This is the hydroxyl groups of the carboxylic acids molecules, when added to water form hydrogen bonds with the surrounding water molecules while the hydrocarbon tail promotes increased order of the adjacent water molecules, similar to that around inert molecules. The addition of the carboxyli acids enhances the structure of the system and causes the viscosity to increase rapidly. This process, however, complete with the opposite process in which the degree of structure is reduced as a result of solute-solvent interactions, as the carboxylic acids concentration in the mixture increases. This gradual breakdown in the solution structure is accompained by a monotonic decrease in viscosity. The appearance of viscosity maximum is to be expected as a result of these process.

We note that, with all alkonoic acids except formic acid, a maximum of viscosity is observed at different molarities. For formic acid + water, viscosity still increases toward higher molarities. This fact also resembles that of F. Kohler[40] who also measured the viscosities of these acids.. This is also because formic acid does not show association, in solution to a large extent. This observation has been confirmed using NMR techniques by H.G. Hertz[13] . However, all other acids exhibit acid-acid association. The association is most conspicuous, when the acid chain is largest. Therefore it may be said that in formic acid, we have uniform random distribution of solvent and solute molecules.

The study of the pure liquid acetic acid including the OH proton interaction shows us that we have the tail on tail configuration with respect to the methyl groups and head on head configuration with respect to the OH protons in analogy to the situation in propionic acid[142]. In aqueous solution we can only study the methyl proton-proton interaction (due to OH proton exchange with the solvent water). We may expect that in acetic acid, when water is added, the same rotation or folding process occurs as described for propionic acid, this the more so as a similar process folding process was also is observed in a mixture of acetic acid with CCl_4[142] and also for propionic acid mixed with CCl_4. However, CH_3COOH dissolved in C_6H_{12} shows much less bending. Taking all these findings together folding seems not to be unique for an aqueous solution of carboxylic acid.

Summarizing, the process of dilution of propionic acid by water is to be described in the following way: Starting from the pure acid, when water is added, the population of the head on head and tail on tail configuration decreases. In other words, the contribution to the first coordination number due to these configuration decreases. Most likely, in particular at low acid concentration, the two pair partners are bound to one another through hydrogen bond. Thus we see that during the dilution process really a folding or rotation of the pair partners relative to one another occurs. In the pure liquid it is reasonable to assume that we have chain like arrangements such that the methyl groups of the two molecules bound by the hydrogen bond are far apart. Probably configuration III as shown on page 78 occurs with high probability, the cyclic form I may also contribute to a minor degree. Of course, a certain degree of bending also takes place. In order to have a realistic picture one should add one or even two molecules to the configuration I and III the axex of which are perpendicular to the plane of the drawing and which are attached to the polar region. Then all alkyl groups point away from the centre of polar coupling[142-14] As more and more water is added, the "star like" arrangement decays and the hydrocarbon parts approach towards one another. The configuration arising at high dilution is in agreement with configuration III as predicted by Schrier Pottle, and Scheraga[143] . The behaviour of acetic acid is similar to that of propionic acid.

The association of carboxylic[142] (i.e. formic, acetic, propionic and butyric acids) in water have also been inferred through intermolecular hydrogen bonding on the bases of studies relating to their viscosity. The hydrogen bond in the association of carboxylic acidsis of $\overset{\leftarrow 2.70\ A^{o} \rightarrow}{0 - H \cdots 0}$ type. In the carboxylic acids containing a methyl group, we found association connected with folding of a given pair of acid molecules may be described as having a head on head and tail on tail configuration, in the water rich region, the bending of H - bonded acid pair increases which leads to a side by side configuration. Now the hydrocarbon of the molecules have less tendency to point away from one another. In a way this finding may be consider to be unexpected, because one might imagine hydrophobic association to occur in the "ideal" form such that we have again tail on tail and head on head configuration. However, now in the reverse sense that is the hydrocarbon rests have direct contact and the carboxylic groups point into the water, thus making a total pair configuration, which is essentially linear.

The system of carboxylic acid and water can be classified as polar and associated[144]. In non electrolyte systems, positive deviations from ideal behaviour are attributed to dispersion forces[145] and negative deviations to the geometric considerations[146]. Attempts have been made to explain the behaviour of liquid mixtures on the basis of sign and magnitude of the excess viscosity η^E and excess volume. ΔV^E.

Examination of figure 13-19 show that the values η^E are positive. As the carboxylic acids concentration is increased the value of η^E reaches a maximum at 0.144,0.873,1.144 and 1.546 of these carboxylic (i.e. formic, acetic, propionic and butyric acids) respectively at 32°C. The maximum appear at 0.4 mole fraction for propionic acid and 0.5 mole fraction for formic acetic and butyric acids respectively. By increasing the temperature from 25°C to 65°C at interval of 5°C. The values of η^E decrease. The maximum values η^E 0.144, 1.110, 1.56 and 1.930 of these carboxylic acids(formic, acetic, propionic and butyric acids) at 25°C decreased to 0.1030, 336, 0.481 and 0.577 at 65°C of these acids respectively. According to Fort and Moore[147] the values of η^E are negative for a system of different molecular size in which dispersion forces are dominant. In our systems the η^E values increase by addition of acid and this show the magnitude of interaction increase with increase in concentration. In the present case all the chemical species being aliphatic, a small difference in size changes the excess viscosity to a large extent. The η^E is more positive for butyric acid than for other acids. For mixture of carboxylic acidswith water for various mole fraction, η^E has the sequence.

Butyric acid > propionic acid >
Acetic acid > formic acid

This trend in the values of η^E give evidence in favour of increasing extent of specific interaction of these acids with water having an increased number of $-CH_2-$ substituents attached to $-\overset{O}{\overset{\|}{C}}-OH$.

In figures 20-26 we compare the magnitude of ΔV^E in the four binary mixture formic acid +water, acetic acid + water, propionic acid + water and butyric acid + water at various temperature from 25°C to 65°C at interval of 5°C. Several effects may contribute[148] to the value of ΔV^E. In the system studied here, we can recognize four different effects as being important:

(1) the breaking of liquid order on mixing;
(2) unfavourable interactions between groups;
(3) differences in molecular volume;
(4) differences in free volume between liquid components;

An effect which is expected to act on ΔV^E in this system, which gives a negative contribution to ΔV^E is difference in molecular size between the two mixture components. Different molecular sizes lead to interstitial accomodation in the mixture and hence to a negative contribution to ΔV^E. The molecules of HCOOH are the smallest of all considered here. Butyric has the largest molar volume 84.68 cm^3 mol^{-1} than other acids whose molar volumes are 37.118 cm^3 mol^{-1}, 51.875 cm^3 mol^{-1} and 71.903 cm^3 mol^{-1} of formic, acetic and propionic acids respectively. The negative contribution to ΔV^E due to interstitia accomodation should be larger in the butyric acid + water mixture. The maximum values for formic, acetic, propionic and butyric acids are 0.114 cm^3 mol^{-1} at 22 M, 0.928 cm^3 mol^{-1} at 14 M, 1.255 cm^{3}mol^{-} at 10 M and 1.603 cm^3 mol^{-1} at 9 M respectively at 32°C. By increasing the temperature the volume contraction (negative value of the excess volume) decrease.

Another effect, also of structural nature, and which again should give a negative contribution to ΔV^E is the difference in free, volume between components. The intermolecular association also contribute to these negative value. The ability of butyric acid to form stronger hydrogen bonds with water are greater as compared to other acids and their sequence are as under

Butyric$>$ Propionic$>$ Acetic$>$Formic

All the systems involved in our previous studied exhibited positive η^E and negative ΔV^E. In the temperature range investigated, the values of $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ are positive and vary in the order butyric acid propionic acid acetic acid formic acid and the values of $\Delta S^{\ddagger}$ are negative. These values are shown in a Table No. 17. The values of $\Delta H^{\ddagger}$ are positive indicating that association and dipole-dipole interactions increase the value of $\Delta H^{\ddagger}$. The values of $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$[149-150] for the mixtures are positive for each binary system studied and increase with increase in acids concentration but for some it decreases. The trends of decline start from 12 M, 10 M and 8 M of acetic, propionic and butyric acids respectively.

VISCOSITY AS A FUNCTION OF CONCENTRATION

Viscosity measurements were made as a function of concentration at different temperatures for formic, acetic, propionic and butyric acids in aqueous solutions. The temperatures for these systems were varied from 25°C to 65°C and concentration range studied was from 0.1 M to 27 M. The figures showing the variation of viscosity with molarity for the above mentioned acids are given figures 1-4. The data reveal that the viscosity as a function of molarity reaches a maximum and then decrease for all acids except formic acid. In the case of formic acid the increase in viscosity with molarity continue until the molarity is 25 and then more or less levels of beyound this concentration. At 65°C, however, the graph shows a small dip in viscosity as the molarity rises beyound the 25 M. In order to described this behaviour, more work is needed for viscosity determination at higher temperature (beyound 65°C). The ensuing discussion embraces the behaviour of acetic, propionic, and butyric acids leaving out the formic acid, because of the reason giving above. The maximum in viscosity for acetic, propionic and butyric acids occur around 14 8 M for the first ~~two~~ acid~~s~~ (i.e. acetic, propionic acids), while at 8 ~~14~~ M for the last acids(i.e. butyric acid). Furthermore, the increase in viscosity with rise in molarity appears more conspicuous as the side chain increase in length.

In order to quantityfy the above statement, it is noted that for acetic acid the peak for viscosity at the highest temperature 65°C is around 0.92 c.p., while the peak for the same acid at 25°C is around 2.32 c.p. giving maximum rise of 1.40 c.p. as the temperature change for 40°C, comparing values for propionic acid (1.53 c.p. 33°C) and butyric acid (1.882 c.p. 37.5°C). The explanation of this behaviour has already been given in terms of acid-acid, water-water, and acid-water interaction. It therefore appears from figure 1 for formic acid that such interaction are at its minimum.

THE VARIATION OF VISCOSITY WITH TEMPERATURE.

Viscosity in centipoise as a function of temperature for all four acids are plotted in figures 5-8. It is noted that the viscosity decreases monotonically with the rise in temperatures for all acids. Again as the concentration is varied for formic acid, the curves remain continuously more or less parallel. The curve for one molar being at the lowest while, for 26.95 molar at the highest. All intermediate concentration lying in between these two curves systematically. However, this trend is not observed for acetic, propionic acid and butyric acids, where curves displacements and crossing occur frequently particularly at higher concentration.

In order to understand fully the behaviour of change of viscosity with temperature, and to calculate the flow activation energy for these systems $\log \eta$ has been plotted against 1/T using equation, 6, figures 9-12.

All acids obey the straight line equation normaly no.6 again formic acid giving parallel lines. For all other acids the lines crossing occur indicating a change in flow activation energy for acetic, propionic, and butyric acids. The flow activation energy for these four systems are given in Table 1.

It appears from the values of flow activation energies, that for formic acid E_η values do not vary much as the molarity rises from 0.1 M to 26.95 M. The computed flow activation energy value for formic acid at 0.1 M equals 1436.04 J mol^{-1}, while the value at approximately 26.95 M is 1456.84 J mol^{-1} such a large change in molarity the flow activation energy only change 20.84 J mol^{-1}. Flow activation energy for other acids show a variation which is more significant. For acetic acid the E_{η} value rises as a function of concentration of 1464.19 J mol^{-1} at 0.1 M reaching a maximum around 14 M with a value 1914.71 J mol and falling back again to 1436.04 J mol^{-1} at 16.95 M concentration Similar trends are shown by propionic and butyric acid , although the trends are more marked here, the over all behaviour appear very much the same. Starting with the minimum E_{η} value of 1531.77 J mol^{-1} at 0.1 M concentration. The maximum of 1994.49 J mol^{-1} is found around 8 M concentration. Finally for butyric acid, the maximum occur around 8 M concentration as well with a value of 2083.04 J mol^{-1}. These values are in line with the argument that the side chain in these acids gradually give large flow activation energies. This can be explained in terms of relaxation of the side chain for acetic, propionic and butyric acids as the concentration rises. The argument made above appear to be valid only if the flow activation energy are temperature independent, which seems to be true in our case, since straight lines of plot $\log\eta$ vs 1/T are more or less uniform. Furthermore the temperature dependent of activation energy is given by Kirchoff[151] equation.

$$\Delta H_{T_1} - \Delta H_{T_2} = \Delta C_p \, (T_2 - T_1),$$

For small temperature change, where $T_2 - T_1$ is of the order of 40°C. The ΔH would vary accordingly.

EXCESS VOLUME AND EXCESS VISCOSITY.

Excess volume and excess viscosity has been calculated using the formulas no. 4 and 5 of Chapter 4. The results have been shown in graphs 13-19 for excess viscosity and graphs 20-26 for excess volume. Here excess quantity (ΔV^E & η^E) are plotted against mole fraction of acids concentration. It seems that as excess volume decreases with the rise of mole fraction of particular acid. The corresponding excess viscosity increases. It is also noted that the effect of temperature on excess viscosity is much more telling than the same effect on ΔV^E. The explanation of this behaviour appears to be in the fact that with the rise in temperature, the intermolecular forces between acid-acid and acid-solvent and solvent-solvent change significantly to effect the viscosity behaviour. While for excess volume, these interactions as a function of temperature seems to go in different directions. This behaviour is well known for liquids containing hydrogen bonds. It is noted that the formation of hydrogen bonds hold molecules at a distance,(hydrogen bond distance being longer than ordinary valence bonds).

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