CHAPTER-III

BARIUM NITRATE IN

METHANOL-WATER SYSTEM

⟨RESULTS AND DISCUSSION⟩

RESULTS AND DISCUSSION :

The relative viscosities and densities of Barium nitrate solutions in 0%, 10%, 20% and 30% by weight of methanol in metahnol-water binary mixtures were determined at 298°, 303°, 308° and 313° K to know the effect of temperature. The concentration range for Barium nitrate was studied from 0.02-0.15 molar. Experiments were designed to include the following studies.

i) Effect of concentration of Barium nitrate on viscosity.

ii) Effect of methyl alcohol percentage on viscosity.

iii) Effect of temperature on viscosity.

iv) The transport properties.

3.1 EFFECT OF CONCENTRATION OF BARIUM NITRATE ON VISCOSITY

The results on the effect of variation of Barium nitrate concentration (0.02-0.15 molar) in metanol-water $(MeOH-H_2O)$ solutions (0%, 10%, 20%, 30%, MeOH w/w) at 298° are given in Table 3.1. It is observed that as the concentration of Barium nitrate increases the viscosity (η), and the relative viscosity (ηr) increases; but the fluidity (ϕ) the reciprocal of viscosity decreases. For Barium nitrate-water solutions (0% methanol) at 298° K the viscosity (η) increases from 0.89167 to 0.91455, the relative viscosity (ηr) increases from 1.00155 to 1.02724 and the fluidity (ϕ) decreases from 1.12147 to 1.09343.

Similar results have been obtained for Barium nitrate in methanol-water $(MeOH-H_2O)$ solution at 303°, 308° and 313° K temperatures (Table 3.2-3.4).

3.2 EFFECT OF METHYL ALCOHOL ON VISCOSITY

At a given temperature (298 $^{\circ}$K) and for a certain concentration of Barium nitrate (say 0.06 M) the viscosity (η) and relative viscosity (ηr) increase as proportion of methyl alcohol (10%, 20%, 30% MeOH-H$_2$O w/w) increases, but the fluidity (ϕ) decreases (Table 3.1).

3.3 EFFECT OF TEMPERATURE ON VISCOSITY :

The data recorded in Table Nos. 3.1-3.4 indicates that the viscosity (η) and relative viscosity (ηr) of Barium nitrate in methanol-water solutions decrese as the temperature increases but the fluididity (ϕ) increase with temperature.

3.4 The viscosity data have been examined in light of following equations.

i) Jones-Dole Equation

ii) Vand Equation

iii) Moulik Equation

iv) Thomas Equation.

According to Jones-Dole equation relative viscosity (ηr) is related to concentration (C) through the relation[76].

$$\eta_r = 1 + A\sqrt{c} + BC \quad \text{-------} \quad (1)$$

Where A and B are the constant[19,77] and C is the concentration of the solute electrolyte in M 1^{-1}. This equation is only applicable to dilute solutions. (C $\leqslant$ 0.1 M)[59]. Franks and Ives[41] carried out exhaustive review and confined attention to monohydric alcohol-water mixtures

which are of greatest interest from the structural view
point. They studied over wide range of concentrations and
concluded that hydrogen bonding which plays a principal role
in the ion-solvent interactions cannot alone account for
additivities in properties that are observed. They surveyed
the properties of the system with special reference to their
structural implications and with the conviction that the
problems concerned must be very significant in many
connections.

Ivanova shan'gina[42] studied viscosity of water-alcohol
solutions of potassium sodium and ammonium nitrates. They
determined the viscosity 'η' of $M.NO_3$ (M = Na, K, NH_4)
solutions in aqueous EtOH and PrOH. They observed that
addition of all salts decreases η of mixed solvents. For 4%
$NaNO_3$, KNO_3 and NH_4NO_3 in H_2O-EtOH, the decrease in η is
1.9, 5.4 and 7.8% respectively. They also interpreted that
NH_4^+ has the greater effect on breaking the solvent
structure.

Therefore it is felt that significant information
regarding solute-solvent interaction can be obtained by
altering the physical properties of solvents without
changing the character and this has been attained by using
mixed solvents namely methanol-water mixtures of varying
compositions.

The theoretical equation of Einstein has been modified
by Vand[51] to represent viscosity of aqueous solutions of
both electrolytes and non-electrolytes at higher
concentrations. The equation may be given as

$$\ln (\eta_r) = \frac{2 \cdot 5 \, \phi}{1 - Q \, \phi} \qquad \text{------} \qquad (2)$$

Where ϕ is volume fraction and is equal to $C\bar{V}$, $\bar{V}$ being the molar volume of electrolyte in solution and Q is the interaction coefficient. The equation of Vand have been rearranged in the linear form as

$$\frac{1}{C} = \left(\frac{0.921}{\bar{V}}\right) \cdot \frac{1}{\log \eta_r} + Q\bar{V} \qquad \text{-----} \quad (3)$$

and the plot of $\dfrac{1}{\log \eta_r}$ Vs $\dfrac{1}{C}$ is the straight line with $Q\bar{V}$ as the intercept and $\dfrac{0.921}{\bar{V}}$ as the slope. S.P. Moulik53 used this equation for different electrolytes and observed that the Vand equation holds a far better way and the calculated values of $\bar{V}$ and Q are nearly equal with the theoretical one.

Further Moulik made a comparative testing of viscosity equations of Vand and Thomas in detail for electrolytes and non-electrolyte solutions. He observed that Thomas equation in its full form is not applicable for majority cases. The equation of Vand is a better relation. For higher concentration of electrolyte he put forward the equation.

$$\eta_r^{?-} = M + K' c^{2-} \qquad \text{-- ------ ---} \quad (4)$$

where M and K' are the constants. The comparative study of these equations over a wide range of concentration for a number of salts has been reported. A single viscosity equation may not be sufficient to cover the viscosity of most aqueous systems containing high fractions of

dissolved solutes. He evaluated the parameters of the equations, which can be used to calculate viscosity of aqueous solutions in the concentration range in which above equation is valid.

Mahapatra, Naik, Misra and Behra[58] measured viscosities of sodium chloride, bromide and iodide in aqueous sucrose solutions of varying concentrations. Sahu and Behra[59] represented the variation of relative viscosity η_r of concentrated aqueous solutions of 1:1 type electrolyte with electrolyte concentration by a general equation by extending the limiting equation of Einstein. Mohanthy and Das[59] determined viscosities of concentrated solutions of potassium chloride and sodium chloride in aqueous urea solutions of varying concentration.

Thomas equation is given as

$$\eta_r = 1 + 2.5\,\phi + 10.05\,\phi^2 \quad - - - - - - (5)$$

Where ϕ is a volume fraction given by $C\overline{V}$ where $\overline{V}$ is the effective rigid molar volume.

Breslau and Miller[56] used the Thomas equation and calculated the molar volumes of a number of aqueous electrolyte solutions. The equation of Thomas has been rearranged in the linear form and used as

$$\frac{\eta_r - 1}{C} = 2.5\,\overline{V} + (10.05\,\overline{V}^2)\,C \quad - - - - - (6)$$

The plot of $\eta_r - 1/C$ Vs C must be linear one; and on this basis the linearity of the results has been tested. Thomas equation is not valid for electrolytes and may not be valid

for many non-electrolytes .

3.4.1 THE JONES - DOLE EQUATION

It has been assumed that the relative viscosities of the electrolyte in binary aqueous solvents like methyl alcohol-water. may be represented by the Jones-Dole equation[76] given below.

$$\eta_r = 1 + A\sqrt{c} + Bc \quad -------(1)$$

Where η_r is the relative viscosity of the solution and 'C' is the molar concentration. 'A' is the Falkenhagen coefficient[19] that takes in to account ionic interactions and 'B' is the Jones-Dole coefficient[77] that is related to the size of the ions and to the different ion-solvent interactions.

The usual procedure to test the validity of the Jones-Dole equation is first to see if a straight line obtained by the plot of $\eta_r - 1/\sqrt{c}$ against $\sqrt{c}$ and from the intercept and slope of the straight line the value of 'A' and 'B' can be obtained respectively. The satisfactory agreement between the calculated value of 'A' and that obtained by the graphical method is a further test of the Jones-Dole equation.

Now in the present communication we have analyzed the data in the light of equation 1. The experimental data recorded in Table 3.1-3.4 shows that Jones-Dole equation is adequate as the plots of $\eta_r - 1/\sqrt{c}$ Vs C are linear as shown in Fig 3.1-3.5. The intercept and slope gave

respectively, the coefficient `A' and `B'. The values of A and B thus obtained are given in Table 3.5 and 3.6 respectively. Values of 'A' and 'B' calculated by least square method are also given in Table 3.5 and 3.6 respectively.

It is seen from Table 3.5 that the values of 'A' coefficent are very small and even negative. The value of 'A' coefficient is found to increase with increase in temperature as well as with methanol composition. The values of 'B' coefficient are all positive and found to decrease with increase in temperature as well as with methanol composition.

From Table 3.1-3.4 it shows that the value of fluidity (ϕ) increases with increase in temperature.

a) 'A' VALUES :

It is evident from Table 3.5 that the value of A is very small and some times it is negative therby indicating very weak ion-ion or solute-solute interactions[78]. The value of A increases with temperature as well as with increase of methanol content at a particular temperature. The electrostatic ion-ion interaction and hence the value of 'A' is found to increase with decrease in dielectric constant, i.e. when the concentration of the organic solvent increases.

b) 'B' VALUES OR COEFFICIENT

To explain the nature of 'B' Cox and Wolfenden[20] have attributed specific additive character to 'B' depending on

the constituent ions. Asmus[21] on the other hand suggests 'B' to be dependent on the lyotropic number and the entropy of hydration of the ionic species present in the medium.

Kaminsky[75] and Gurney[79] have suggested that 'B' (in Jones-Dole equation) is a measure of ion-dipole interaction between the ion and the solvent molecules and have supported the idea of partitioning the 'B' coefficients to their ionic components assuming that the 'B' components of potassium and chloride ions are equal in potassium chloride. When such interaction is considered, the magnitude of 'B' is dependent on the manner and the extent to which the ions orient the water dipole in their cospheres at a particular temperature.

It is evident from Table 3.6 that B - coefficients are all positive but small in magnitude and decrease with increase in temperature as well as with increase in methanol content at a particular temperature.

B - coefficient is an adjustable parameter either positive or negative and is said to be a measure of effective hydrodynamic volume of solvated ions that accounts for ion-solvent interaction[80]. It is also known as a measure of order or disorder introduced by ions in the solvent structure.

Recently it has been emphasized by a number of workers that dB/dT is a more important criterion[74] for determining the solute-solvent interactions. Viscosity study of a number of such solutions has shown that structure makers will have negative values of dB/dT and structure-breakers

positive values. Accordingly, in the present case the negative temperature coefficient of B, in 0, 10, 20 and 30% methanol-water, suggests that Barium nitrate behaves as a structure maker/promoter.

C) THE CONCEPT OF STRUCTURE-MAKING AND STRUCTURE-BREAKING EFFECT OF SOLUTES[74]

According to the hypothesis given above, the water molecules can be considered to be in dynamic equilibrium between the bulky tetrahedrally hydrogen-bonded clusters and the denser monomer molecules, as represented by $(H_2O)b \rightleftharpoons (H_2O)d$ and the statistical degree of ice-likeness (or whatever its structure in water is) is considered to be proportional to the half-life of the clusters, which is of the order of 10^{-11} s in pure water[81]. When a solute is put into water, it is assumed that the former may shift the equillibrium in either direction. A solute which causes a shift so as to increase the number and the average half-life of the cluster is termed a sturctre-maker, and a solute which has an effect in the opposite direction is called a structure-breaker[81]. Although the concept of structure-making and breaking effects of solutes is not entirely satisfactory, it has proved useful in discussing the effects of solutes on water structure. These effects can be detected experimentally by observing the changes brought about by the solutes in the properties of water, such as fluidity, reorientation time, viscosity, conductance and heat capacity. For instance structure-makers are shown

to decrease the fluidity of water (by causing an increase in reorientation time and increase in viscosity) and result in positive excess partial molal heat capacities in water. The reverse is true for structure-breakers.

Frank and Wen in order to explain these phenomena, visualized[81] a picture (See Figure 3.1a and 3.1b) in which an ion is surrounded by concentric regions of water molecules. The innermost region 'A' consists of water molecules polarized, immobillized, and electrostricted by the ion. The water molecules in the region C have the normal liquid structure which is polarized in the usual way by the ionic field which at this range will be relatively weak. The intermediate region B is the region in which water is less ice-like, i.e. more randomly ordered than the normal water. The decreased structure in this region is presumably due to the approximate balance of two competing forces, namely the normal structre-Orientating influence of the neighbouring water molecules, and the radially orienting influence of the electric field of the ion, which act simultenously on any water molecule in this region. The latter ionic influence predominates in the region A and the former in region C, and between A and C there should be a region of finite width in which more orientational disorder should exist than in either A or C. Now, it was assumed in the flickering cluster model[81] of water that the lifetime of a cluster is essentially dependent on the fluctuations of energy produced in the liquid water. An ion with its first layer of water molecules will be a disturbing centre which
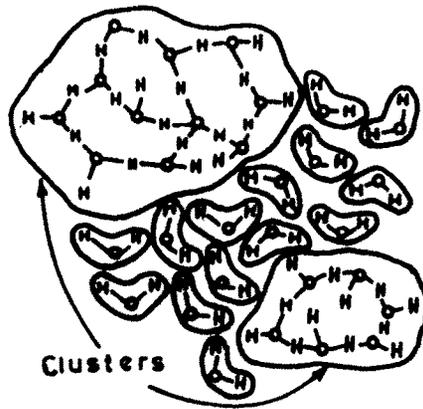
FIG. 3·1 a — FRANK–WEN FLICKERING CLUSTER
MODEL OF LIQUID WATER.

Primary hydration
H_2O irrotationally
bound.

Normal liquid H_2O

Disorganized H_2O
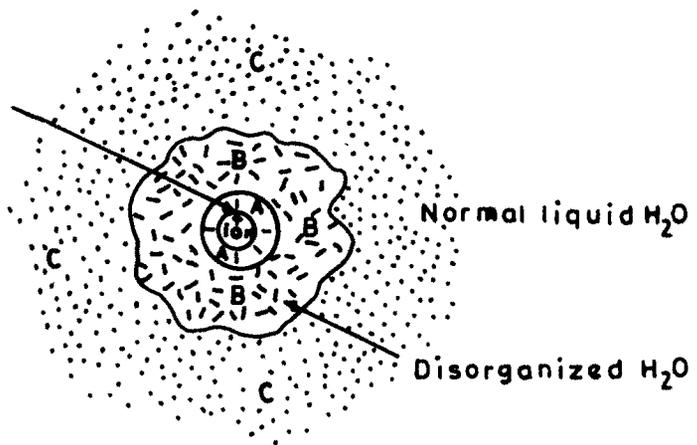
FIG. 3·1 b — FRANK–WEN ZONE MODEL OF WATER

IN THE NEIGHBOURHOOD OF A

SIMPLE ION.

would both interfere with the initiation of clusters and hasten their disruption. Ions with low charge-density have relatively weak electrostatic fields which makes the region `A ' very small thereby causing net decrease in structure. In the case of structure-making ions of high charge-density, the region A of immobilization exceeds region B which results in a net structural increase around these ions.

d) UNDERLINE DEPENDENCE OF 'B' ON TEMPERATURE :

According to Stokes and Mills[49], the viscosity of dilute electrolytic solutions incorporates that of the solvent and the contribution from other sources. They are η_E, the positive increase due to the shape and size of the ion, η_A, the increase due to the alignment or orientation of the polar molecules by the ionic field and η_D, the decrease in viscosity arising out of the distortion of the solvent structure. Therefore 'B' coefficients can be discussed in terms of these viscosity effects at different temperatures.

Kaminsky[75] has related negative temperature coefficient of 'B' to the fact that oriented water molecules in the secondary layer will be less rigidly held due to increased thermal motion. This will give a significant decrease in η_A. However, in spite of this decrease the sum of $\eta_E + \eta_A$ will still be larger than η_D because with increasing temperature η_D will decrease due to less competition between the ionic field and the reduced solvent structures. η_E will remain fairly constant and η_A will decrease fairly slowly so that, eventually $\eta_E + \eta_A > \eta_D$ and 'B' will be positive.

Nightingale[32] also suggests that hydration may increase as the water structure is broken down but it is arguable that the increased thermal motion would counteract this tendency. It may be added that there is no thermodynamic evidence to support increased hydration.

e) DEPENDENCE OF 'B' ON METHANOL CONTENT :

The decrease in 'B' coefficient with increase in methanol content in the solvent mixture (Table 3.6) may be attributed to the small size of the solvent molecules and also to the weak association between water and methanol through hydrogen bonding[77] and for solvated ions it would lead to smaller values of η_E and η_A. Consequently the 'B' coefficient becomes smaller and smaller with the increase in methanol content in the medium.

3.4.2 VAND EQUATION :

The viscosity data have been examined in the light of Vand[54] equation, which may be given as

$$\frac{1}{C} = \frac{0.921}{\overline{V}} \cdot \frac{1}{log\,\eta_r} + Q\overline{V} \quad ----\ (3)$$

In this equation Q is an interation parameter dealing with mutual interference between the spheres and their Brownian motion and $\overline{V}$ is the effective rigid molar volume of solute in $dm^3\,mol^{-1}$. The viscosity cannot be calculated without having knowledge of these viscosity parameters. The up-to-date knowledge does not permit to evaluate them theoretically. Therefore graphical testing is the only other alternative of proving. This has been performed in

the present work.

The applicability of the Vand equation has been tested from the linear plots of

$$\frac{1}{\log \eta_r} \quad Vs \quad \frac{1}{c}$$

Plots are drawn using data given in Table 3.7-3.10. The plots of $\frac{1}{\log \eta_r}$ Vs $\frac{1}{c}$

shown in Figs 3.6-3.9 are linear in the concentration range 0.06 - 0.15 M. The viscosity parameters Q and $\bar{V}$ calculated by graphical method are given in Tables 3.11.a and 3.11.b respectively. The parameters may be useful to calculate the viscosity of solutions.

From Table Nos. 3.11.a and 3.11.b it has been noticed that molar volume $(\bar{V})$ and the interaction coefficient (Q) both increase with temperature and methanol concentration. This may be ascribed to the increase in the electrostatic attraction between water dipole and the ion as large number of water molecules become available in the consphere of the ions due to thermal agitation[58].

On the basis of the increase in the value of $\bar{V}$ of Barium nitrate in methanol solutions it can be inferred that the ions get more and more hydrated in the presence of methanol. In Einstein's[83] treatment of viscosity of dilute solutions the ions are treated as rigid spheres. The ionic molar volume $\bar{V} \pm$ can be obtained from Equation

$$B \pm = 2.5\, \bar{V} \pm \qquad ----------- (7)$$

where 2.5 is the shape factor for sphere and $B \pm$ values calculated according to the procedure of Kaminsky[35]. We

may assume that the ions in methanol solutions due to their greater affinity for water dipole in the microscopic region, behave as rigid hard spheres. Barium nitrate promotes the solvent structure around ion[59] indicates that Barium nitrate is structure maker.

The structure-making[57] ions have positive ionic molar volumes $(\overline{V}_\pm)$ and hydration numbers (NB) and structure breaking ions have negative ionic molar volumes $(\overline{V}_\pm)$ and hydration numbers in solution. Hydration numbers (NB) of ions can be obtained from the equation

$$\overline{V} \pm = \overline{V}_0 \text{ ion} + NB\ \overline{V}_s^0 \quad - - - - - - - - - - - - - (3)$$

where $\overline{V}^\circ$ ion is the free ionic volume calculated from the equation $\overline{V}^\circ$ ion $= 2.52\ r^3$ (r = ionic radius) and $\overline{V}_s^0$ is the molar volume of water equal to 6.62 cm^3 mol^{-1}. The hydration numbers of positive and negative ions bear different linear relationships with their ionic $B_\pm$ coefficients. This supports the idea that structure-making ions have positive ionic molar volumes, positive hydration numbers and positive entropy changes while structure-breaking ions have negative ionic molar volumes hydration numbers and negative entropy changes in aqueous solutions.

The idea of positive and negative hydration[84] and hence the positive and negative hydration numbers get support from the work of Angel[85].

The values of ionic parameters at 298 K in 0% methanol water solutions are given in Table 4.15. From Table 4.15 it is seen that ionic parameter values of Ba^{++} ion are all

positive. This supports the idea[84,85] that Ba^{++} is
electrostictive structure making ion with positive ionic
volume $(\bar{V}_\pm)$, hydration number (NB) and entropy charge
(ΔS).

3.4.3 MOULIK EQUATION :

It has been observed[83] that the relative viscosities of
the electrolytic solutions in binary aqueous solvents like
methyl alcohol-water may be represented by the Moulik
Equation given below

$$\eta_r^2 = M + K'c^2 \qquad ----- \qquad (4)$$

Where M and K' have their usual physical significance. It
can be seen from the equation (4) that viscosity cannot be
calculated without having knowledge of constants M and K'.
These parameters cannot be evaluated theoretically
therefore, graphical testing has been performed. This has
been performed in the present work. The evaluated
parameters may be useful to calculate the viscosity of
solutions.

The applicability of the Moulik equation has been
tested from the linear plots of η_r^2 Vs C^2. The plots
are drawn using the data given in Table No. 3.7-3.10. The
plots of η_r^2 Vs C^2 are shown in Fig 3.10-3.13. Plots
are seen to be not linear below 0.1 M concentration.
Therefore Moulik equation seems to be invalid below 0.1M
concentration. The intercepts and slopes of straight line
plots yield M and K' respectively.

The viscosity parameters M and K' has been calculated by graphical method and are given in Tables 3.12.a and 3.12.b respectively. From Table No. 3.12.a it has been noticed that constant M increases with increase in temperature and concentration of methyl alcohol. From Table 3.12.b it is seen that the constant K' decreases with increase in temperature and concentration of methyl alcohol.

3.4.4] <u>THOMAS</u> <u>EQUATION</u> :

For higher concentration of electrolyte Thomas[86] put forward the equation as

$$\eta_r = 1 + 2 \cdot 5 \, \phi + 10 \cdot 05 \, \phi^2 \text{ ------ } (5)$$

Where ϕ is a volume fraction given by $C\overline{V}$ where $\overline{V}$ is the effective rigid molar volume. Therefore the equation (5) becomes

$$\frac{\eta_r - 1}{C} = 2 \cdot 5 \, \overline{V} + (10 \cdot 05 \, \overline{V}^2) \, C \text{ ----- } (6)$$

Where C is the molar concentration.

The applicability of Thomas equation has been tested from the linear plots of $\frac{\eta_r - 1}{C}$ Vs C. Plots are drawn from the data given in Table 3.7-3.10. The plots of $\frac{\eta_r - 1}{C}$ Vs C are shown in Fig 3.14-3.17. The plots are not linear therefore Thomas equation is not valid for Barium nitrate in the concentration range 0.02 - 0.15 M. From the results of Moulik[54] it also indicates that Thomas equation in its full form, is not valid for electrolytes and may not be valid also for many non electrolytes.

3.5 THE TRANSPORT PROPERTIES : (ACTIVATION PARAMETERS)

The interpretation of viscous flow according to the theory of absolute reaction rates has been presented by Eyring and co-workers[55] . Nightingale and Benck[62] and Feakins[87] have shown that the theory of reaction rate can be successfully applied to electrolyte solutions. Nightingale calculated the activation energy 'ΔE^* '(which does not differ appreciably from activation enthalpy), free energy of activation 'ΔF^* ' and the entropy of activation 'ΔS^* ' for water and a number of electrolytic solutions.

The energy of activation for viscous flow ΔE^* is given by

$$\Delta E^* = R \ \frac{d \ln \eta}{d \ (1/T)} \qquad - - - - - - - - - (7)$$

The plot of ln η Vs 1/T is linear and ΔE^* can be calculated as

$$\Delta E^* = \text{slope} \times R$$

In a similar manner the free energy of acitivation for viscous flow is given by[55]

$$\Delta F^* = RT \ln \ \frac{\eta \ V}{h \ N}$$

Where h is the Planck constant and N is the Avogadro number. V may be regarded as the volume of one mole of solution particles and is given by

$$V = \frac{1000}{n_1 + \nu n_2} \quad \text{cm3}$$

Where ν is the number of species into which a solute molecule dissociates and n_2 is the number of moles of solute

per litre of solution.   The number of moles of solvent, n_1, per litre of solution is given by

$$n_1 = \frac{1000\,\rho - n_2\,M_2}{M_1}$$

Where M_1 and M_2 are the molecular weights of the solvent and solute, respectively.   Assuming that the activation enthalpy does not differ appreciably from the activation energy, the entropy of activation ΔS^* may also be calculated as

$$\Delta S^* = (\Delta E^* - \Delta F^*) / T$$

Proceeding along similar lines, energy of activation (ΔE^*) the free energy of activation (ΔF^*) and entropy of activation (ΔS^*) have been calculated for the solvents and for Barium nitrate (C = 0.1 MOLE/L) in different Wt. % of methanol at 298 $^{\circ}$K.   The results are recorded in table No. 3.13.

From Table No,. 3.13 it is seen that the energy and entropy of activation of the viscous flow of solution are more than those of solvent.   When ΔE^* and ΔS^* of viscous flow are less than that of solvent indicates solute-solvent interaction and when ΔE^* and ΔS^* of viscous flow are more than that of solvent indicates little solute solvent interaction[27,28,30].   In our calculations ΔE^* and ΔS^* of viscous flow of solutions are more than that of solvents shows that there is little solute-solvent interaction.

According to D.K. Dash and P.B. Das[37] when ΔE^* , ΔF^* and ΔS^* values are less than that of solvent it indicates structure breaking effect and when ΔE^* , ΔF^* and ΔS^* values

are more than solvent indicates structure making effect. They have studied thermodynamic properties of Cadmium nitrate and strontium nitrate in different weight proportions of methanol at 308 K. According to them ΔE^*, ΔS^* and ΔF^* values of viscous flow of solutions are less than that of solvents indicating structure breaking effect. In our data ΔE^*, ΔS^* and ΔF^* of viscous flow are more than that of solvent indicates structure making effect of Barium nitrate.

The abnormally large energies and entropies of activation are characteristic of associated liquids and are attributed to the excess energy necessary to break the hydrogen bonds in the solutions [55].

In the case of Barium nitrate ΔE^* and ΔS^* values are higher than those of solvent in all solvent compositions. NO_3^- ion have structure breaking [75] properties. Therefore from above results it clearly indicates that due to the presence of Ba^{++}, the solvent structure is stabilised or in other words the Ba^{++} not only associates with the solvent molecule in the co-sphere and stabilises the solvent structure but also predominates over the sturcture breaking properties of its partner [26].

The Thermodynamic parameters of viscous flow of Barium nitrate in 10% methanol-water solution are calculated [55] at 298 K. The values are presented in Table 3.14. These results are in agreement with results of H. Macdonald, G. Marangoni and R. Palepu [88]. They have discussed the

dependence of thermodynacmic parameters of viscous flow $(\Delta E^*$, ΔS^* and ΔF^*) on concentration of structure-making electrolytes and structure-breaking electrolytes. According to them in case of structure-making electrolyte ΔE^* of viscous flow remains constant with an increase in concentration of the electrolyte, ΔS^* decreases and ΔF^* increases slightly. It is seen from Table 3.14 that ΔE^* of viscous flow remains constant with an increase in concentration of Barium nitrate, ΔS^* decreases and ΔF^* increases slightly. It indicates that Barium nitrate is structure-maker.

Table 3.1

VISCOSITY DATA FOR BARIUM NITRATE IN DIFFERENT METHANOL - WATER COMPOSITIONS AT 298° k.

concentration moles/lit	$(conc^n)^{1/2}$	η mNSm^{-2}	ηr	ϕ	$\frac{\eta r-1}{\sqrt{c}}$
Wt. % MeOH in MeOH-H_2O = 0					
0.02	0.1414	0.89167	1.00155	1.12147	0.011
0.04	0.2	0.89492	1.00519	1.11741	0.026
0.06	0.2449	0.89841	1.00911	1.11307	0.037
0.08	0.2828	0.90213	1.01329	1.10848	0.047
0.1	0.3162	0.90589	1.01752	1.10387	0.055
0.12	0.3464	0.90958	1.02166	1.09940	0.0625
0.15	0.3873	0.91455	1.02724	1.09343	0.070
Wt. % MeOH in MeOH-H_2O = 10					
0.02	0.1414	1.14901	1.00247	0.87031	0.0175
0.04	0.2	1.15236	1.00540	0.86777	0.027
0.06	0.2449	1.15600	1.00857	0.86505	0.035
0.08	0.2828	1.15995	1.01202	0.86210	0.0425
0.1	0.3162	1.16360	1.01520	0.85940	0.048
0.12	0.3464	1.16734	1.01847	0.85664	0.053
0.15	0.3873	1.17274	1.02318	0.85269	0.06
Wt. % MeOH in MeOH-H_2O = 20					
0.02	0.1414	1.38955	1.00424	0.71965	0.030
0.04	0.2	1.39472	1.00801	0.71698	0.040

0.06	0.2449	1.40019	1.01192	0.71418	0.0485
0.08	0.2828	1.40529	1.01561	0.71159	0.055
0.1	0.3162	1.41010	1.01909	0.70916	0.061
0.12	0.3464	1.41483	1.02251	0.70679	0.065
0.15	0.3837	1.42200	1.02769	0.70323	0.0715

Wt. % MeOH in MeOH.H$_2$O = 30

0.02	0.1414	1.53926	1.00480	0.64966	0.034
0.04	0.2	1.54447	1.00822	0.64747	0.041
0.06	0.2449	1.54912	1.01123	0.64552	0.046
0.08	0.2828	1.55342	1.01404	0.64374	0.0495
0.1	0.3162	1.55787	1.01694	0.64190	0.0555
0.12	0.3464	1.56247	1.01992	0.64001	0.0575
0.15	0.3873	1.56869	1.02401	0.97655	0.06

Table 3.2

VISCOSITY DATA FOR BARIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 303 $^{\circ}$K.

concentration moles/lit	$(conc^n)^{1/2}$	η mNS m^{-2}	η_r	ϕ	$\dfrac{\eta_r-1}{\sqrt{c}}$
Wt. % MeOH in MeOH-H_2O = 0					
0.02	0.1414	0.79919	1.00212	1.25126	0.015
0.04	0.2	0.80199	1.00564	1.24689	0.028
0.06	0.2449	0.80482	1.00918	1.24251	0.375
0.08	0.2828	0.80787	1.01301	1.23782	0.046
0.1	0.3162	0.81099	1.01692	1.23306	0.0535
0.12	0.3464	0.81420	1.02095	1.22819	0.0605
0.15	0.3873	0.81912	1.02711	1.22082	0.070
Wt. % MeOH in MeOH-H_2O = 10					
0.02	0.1414	1.02036	1.00354	0.98004	0.025
0.04	0.2	1.02350	1.00662	0.97703	0.033
0.06	0.2449	1.02673	1.00980	0.97396	0.04
0.08	0.2828	1.02956	1.01258	0.97128	0.0445
0.1	0.3162	1.03251	1.01549	0.96851	0.049
0.12	0.3464	1.03542	1.01835	0.96579	0.053
0.15	0.3873	1.03979	1.02265	0.96173	0.0585
Wt % MeOH in MeOH.H_2O = 20					
0.02	0.1414	1.21349	1.00558	0.82406	0.0395
0.04	0.2	1.21811	1.00941	0.82094	0.047
0.06	0.2449	1.22226	1.01285	0.81815	0.0525

0.08	0.2828	1.22620	1.01611	0.81552	0.057
0.1	0.3162	1.23002	1.01928	0.81299	0.061
0.12	0.3464	1.23371	1.02274	0.81056	0.0645
0.15	0.3873	1.23924	1.02692	0.80694	0.0695

Wt. % MeOH in MeOH.H_2O = 30

0.02	0.1414	1.32366	1.00580	0.75548	0.041
0.04	0.2	1.32844	1.00943	0.75276	0.047
0.06	0.2449	1.33245	1.01248	0.75049	0.051
0.08	0.2828	1.33649	1.01555	0.74822	0.055
0.1	0.3162	1.34015	1.01833	0.74618	0.058
0.12	0.3464	1.34383	1.02113	0.74414	0.061
0.15	0.3873	1.34890	1.02498	0.74134	0.0645

Table 3.3

VISCOSITY DATA FOR BARIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 308 $^\circ$ K.

concen tration moles/lit	$(conc)^{n^{1/2}}$	η $mNSm^{-2}$	η_r	ϕ	$\dfrac{\eta_r-1}{\sqrt{c}}$
Wt. % MeOH in MeOH.H$_2$O = 0					
0.02	0.1414	0.72222	1.00392	1.38461	0.028
0.04	0.2	0.72499	1.00778	1.37931	0.039
0.06	0.2449	0.72751	1.01128	1.37454	0.046
0.08	0.2828	0.73042	1.01532	1.36907	0.054
0.1	0.3162	0.73335	1.01940	1.36359	0.061
0.12	0.3464	0.73632	1.02352	1.35810	0.068
0.15	0.3873	0.74047	1.02930	1.35047	0.0755
Wt. % MeOH in MeOH.H$_2$O = 10					
0.02	0.1414	0.90315	1.00505	1.10723	0.036
0.04	0.2	0.90634	1.00860	1.10333	0.043
0.06	0.2449	0.90927	1.01187	1.09978	0.0485
0.08	0.2828	0.91195	1.01485	1.09655	0.0525
0.1	0.3162	0.91480	1.01802	1.09313	0.057
0.12	0.3464	0.91761	1.02113	1.08978	0.061
0.15	0.3873	0.92212	1.02614	1.08445	0.0675
Wt. % MeOH in MeOH.H$_2$O = 20					
0.02	0.1414	1.06878	1.00721	0.93564	0.051
0.04	0.2	1.07340	1.01157	0.93161	0.575
0.06	0.2449	1.07711	1.01506	0.92841	0.615

0.08	0.2828	1.08107	1.01880	0.92500	0.0665
0.1	0.3162	1.08444	1.02197	0.92213	0.0695
0.12	0.3434	1.08749	1.02511	0.91954	0.0725
0.15	0.3873	1.09235	1.02943	0.91545	0.076

Wt. % MeOH in MeOH-H_2O = 30

0.02	0.1414	1.16134	1.00770	0.86107	0.0545
0.04	0.2	1.16613	1.01186	0.85753	0.059
0.06	0.2449	1.16996	1.01518	0.85973	0.062
0.08	0.2828	1.17365	1.01838	0.85204	0.065
0.1	0.3162	1.17706	1.02134	0.84957	0.0775
0.12	0.3464	1.18041	1.02425	0.84716	0.07
0.15	0.3873	1.18483	1.02808	0.84400	0.0725

Table 3.4

VISCOSITY DATA FOR BARIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 313 $^{\circ}$K.

concentration moles/lit	$(conc)^{1/2}$	η mNSm^{-2}	η_r	ϕ	$\dfrac{\eta_r - 1}{\sqrt{c}}$
Wt. % MeOH in MeOH-H$_2$O = 0					
0.02	0.1414	0.65705	1.00605	1.52195	0.043
0.04	0.2	0.65978	1.01023	1.51565	0.051
0.06	0.2449	0.66225	1.01402	1.50998	0.057
0.08	0.2828	0.66456	1.01756	1.50473	0.062
0.1	0.3162	0.66699	1.02128	1.49925	0.067
0.12	0.3464	0.66937	1.02492	1.49393	0.072
0.15	0.3873	0.67313	1.03068	1.48558	0.079
Wt. % MeOH in MeOH-H$_2$O = 10					
0.02	0.1414	0.80831	1.00721	1.23714	0.051
0.04	0.2	0.81138	1.01104	1.23246	0.055
0.06	0.2449	0.81420	1.01456	1.22818	0.0595
0.08	0.2828	0.81693	1.01795	1.22409	0.0635
0.1	0.3162	0.81965	1.02134	1.22003	0.0675
0.12	0.3464	0.82197	1.02424	1.21657	0.070
0.15	0.3873	0.82567	1.02885	1.21112	0.0745
Wt. % MeOH in MeOH-H$_2$O = 20					
0.02	0.1414	0.94907	1.00834	1.05366	0.059
0.04	0.2	0.95330	1.01283	1.04898	0.064
0.06	0.2449	0.95689	1.01665	1.04505	0.068

0.08	0.2828	0.96011	1.02007	1.04154	0.071
0.1	0.3162	0.96310	1.02324	1.03831	0.0735
0.12	0.3464	0.96584	1.02615	1.03536	0.0755
0.15	0.3873	0.97038	1.03098	1.03052	0.08

Wt. % MeOH in MeOH-H_2O = 30

0.02	0.1414	1.02363	1.00856	0.97691	0.0605
0.04	0.2	1.02800	1.01286	0.97276	0.064
0.06	0.2449	1.03147	1.01628	0.96949	0.0665
0.08	0.2828	1.03475	1.01951	0.96641	0.069
0.1	0.3162	1.03773	1.02245	0.96364	0.071
0.12	0.3464	1.04060	1.02528	0.96098	0.073
0.15	0.3873	1.04463	1.02924	0.97159	0.0755

Table 3.5 A . $10^3/1^{1/2}$. $mol^{-1/2}$

Mass fraction of methanol Temperature (^{o}K)	0%	10%	20%	30%
298	-0.024 (-0.024)	-0.007 (-0.007)	0.006 (0.004)	0.019 (0.017)*
303	-0.016 (-0.016)	0.006 (0.005)	0.023 (0.022)	0.028 (0.027)
308	0.002 (0.001)	0.019 (0.019)	0.037 (0.036)	0.044 (0.044)
313	0.024 (0.023)	0.037 (0.036)	0.042 (0.047)	0.053 (0.052)

* Values given in brackets are obtained by least square method.

Table 3.6 B/1 mol^{-1}

Mass fraction of methanol Temperature (^{o}K)	0%	10%	20%	30%
298	0.25 (0.252)	0.189 (0.174)	0.176 (0.178)	0.135 (0.118)*
303	0.221 (0.219)	0.138 (0.137)	0.122 (0.122)	0.111 (0.097)
308	0.189 (0.186)	0.121 (0.119)	0.108 (0.106)	0.075 (0.074)
313	0.134 (0.136)	0.095 (0.094)	0.083 (0.083)	0.056 (0.06)

* Values obtained by least square method are given in brackets.

Table 3.7

VISCOSITY DATA FOR BARIUM NITRATE IN 0 % METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.

Temperature (oK)	concentration (C) moles/lit	$\frac{1}{C}$	c^2	$\frac{1}{\log \eta_r}$	η_r^2	$\eta_r - 1/c$
	0.02	50.00	0.0004	1486.7	1.003	0.077
	0.04	25.00	0.0016	444.8	1.010	0.129
	0.06	16.66	0.0036	253.9	1.018	0.152
298	0.08	12.50	0.0064	174.4	1.027	0.166
	0.1	10.00	0.01	132.6	1.035	0.175
	0.12	8.33	0.0144	107.5	1.044	0.180
	0.15	6.66	0.0225	85.6	1.055	0.181
	0.02	50.00	0.0004	1087.3	1.004	0.106
	0.04	25.00	0.0016	409.4	1.011	0.141
	0.06	16.66	0.0036	251.9	1.018	0.153
303	0.08	12.50	0.0064	178.1	1.026	0.163
	0.1	10.00	0.01	137.2	1.034	0.169
	0.12	8.33	0.0144	110.0	1.042	0.176
	0.15	6.66	0.0225	86.8	1.055	0.181
	0.02	50.00	0.0004	588.5	1.008	0.196
	0.04	25.00	0.0016	297.1	1.016	0.195
	0.06	16.66	0.0036	205.2	1.023	0.188
	0.08	12.50	0.0064	151.4	1.031	0.192
308	0.1	10.00	0.01	119.8	1.039	0.194

	0.12	8.33	0.0144	99.0	1.048	0.196
	0.15	6.66	0.0225	79.7	1.059	0.195
	0.02	50.00	0.0004	381.7	1.012	0.302
	0.04	25.00	0.0016	226.2	1.021	0.255
	0.06	16.66	0.0036	165.3	1.028	0.233
313	0.08	12.50	0.0064	132.2	1.032	0.219
	0.1	10.00	0.01	109.3	1.043	0.212
	0.12	8.33	0.0144	93.5	1.050	0.207
	0.15	6.66	0.0225	76.2	1.062	0.204

Table 3.8

VISCOSITY DATA FOR BARIUM NITRATE IN 10% METHANOL-WATER
SOLUTION AT DEFFERENT TEMPERATURES.

Temperature (oK)	concentration (C) moles/lit	$\frac{1}{C}$	C^2	$\frac{1}{\log \eta_r}$	η_r^2	$\eta_r - 1 / c$
	0.02	50.00	0.0004	933.3	1.005	0.123
	0.04	25.00	0.0016	427.5	1.011	0.135
	0.06	16.66	0.0036	269.8	1.017	0.142
298	0.08	12.50	0.0064	192.7	1.024	0.150
	0.1	10.00	0.01	152.6	1.031	0.152
	0.12	8.33	0.0144	125.8	1.037	0.154
	0.15	6.66	0.0225	100.5	1.047	0.154
	0.02	50.00	0.0004	651.6	1.007	0.177
	0.04	25.00	0.0016	348.9	1.013	0.165
	0.06	16.66	0.0036	236.1	1.020	0.163
303	0.08	12.50	0.0064	184.1	1.025	0.157
	0.1	10.00	0.01	149.8	1.031	0.155
	0.12	8.33	0.0144	126.6	1.037	0.153
	0.15	6.66	0.0225	102.8	1.046	0.151
	0.02	50.00	0.0004	457.1	1.018	0.252
	0.04	25.00	0.0016	268.9	1.017	0.215
	0.06	16.66	0.0036	195.1	1.024	0.197
308	0.08	12.50	0.0064	156.2	1.030	0.185
	0.1	10.00	0.01	128.9	1.036	0.180

	0.12	8.33	0.0144	110.1	1.043	0.176
	0.15	6.66	0.0225	89.2	1.053	0.174

	0.02	50.00	0.0004	320.5	1.014	0.360
	0.04	25.00	0.0016	209.7	1.022	0.276
	0.06	16.66	0.0036	159.3	1.029	0.242
313	0.08	12.50	0.0064	129.4	1.036	0.224
	0.1	10.00	0.01	109.0	1.043	0.213
	0.12	8.33	0.0144	96.1	1.049	0.202
	0.15	6.66	0.0225	80.9	1.059	0.192

Table 3.9

VISCOSITY DATA FOR BARIUM NITRATE IN 20% METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.

Temperature (oK)	concentration (C) moles/lit	$\dfrac{1}{C}$	C^2	$\dfrac{1}{\log \eta_r}$	η_r^2	$\eta_r - 1/C$
	0.02	50.00	0.0004	544.2	1.008	0.212
	0.04	25.00	0.0016	288.6	1.016	0.200
	0.06	16.66	0.0036	194.3	1.024	0.198
298	0.08	12.50	0.0064	148.7	1.031	0.195
	0.1	10.00	0.01	121.8	1.039	0.191
	0.12	8.33	0.0144	103.4	1.046	0.187
	0.15	6.66	0.0225	84.3	1.056	0.184
	0.02	50.00	0.0004	413.8	1.011	0.279
	0.04	25.00	0.0016	245.8	1.019	0.235
	0.06	16.66	0.0036	180.3	1.026	0.214
303	0.08	12.50	0.0064	144.1	1.032	0.201
	0.1	10.00	0.01	120.6	1.039	0.192
	0.12	8.33	0.0144	102.4	1.046	0.189
	0.15	6.66	0.0225	86.7	1.055	0.179
	0.02	50.00	0.0004	320.5	1.014	0.360
	0.04	25.00	0.0016	200.2	1.023	0.289
	0.06	16.66	0.0036	154.0	1.030	0.251
308	0.08	12.50	0.0064	123.6	1.038	0.235
	0.1	10.00	0.01	105.9	1.044	0.219

	0.12	8.33	0.0144	92.8	1.051	0.209
	0.15	6.66	0.0225	79.4	1.060	0.196

	0.02	50.00	0.0004	277.2	1.017	0.417
	0.04	25.00	0.0016	180.6	1.026	0.320
	0.06	16.66	0.0036	139.4	1.036	0.277
313	0.08	12.50	0.0064	115.9	1.041	0.250
	0.1	10.00	0.01	100.2	1.047	0.232
	0.12	8.33	0.0144	89.2	1.053	0.218
	0.15	6.66	0.0225	75.5	1.063	0.206

Table 3.10

VISCOSITY DATA FOR BARIUM NITRATE IN 30% METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURES.

Temperature (oK)	concentration (C) moles/lit	$\dfrac{1}{C}$	c^2	$\dfrac{1}{\log \eta_r}$	η_r^2	$\eta_r - 1/c$
	0.02	50.00	0.0004	480.8	1.010	0.240
	0.04	25.00	0.016	281.3	1.017	0.205
	0.06	16.66	0.0036	206.2	1.023	0.187
298	0.08	12.50	0.0064	165.2	1.028	0.175
	0.1	10.00	0.01	137.1	1.034	0.169
	0.12	8.33	0.0144	116.7	1.039	0.158
	0.15	6.66	0.0225	97.0	1.046	0.160
	0.02	50.00	0.0004	398.1	1.012	0.290
	0.04	25.00	0.0016	245.3	1.019	0.235
	0.06	16.66	0.0036	185.6	1.025	0.208
	0.08	12.50	0.0064	149.2	1.031	0.194
303	0.1	10.00	0.01	126.8	1.037	0.183
	0.12	8.33	0.0144	110.1	1.043	0.176
	0.15	6.66	0.0225	93.3	1.051	0.166
	0.02	50.00	0.0004	300.2	1.015	0.385
	0.04	25.00	0.0016	195.3	1.024	0.296
	0.06	16.66	0.0036	152.8	1.031	0.253
	0.08	12.50	0.0064	126.4	1.037	0.229
308	0.1	10.00	0.01	109.0	1.043	0.213

	0.12	8.33	0.0144	96.1	1.049	0.202
	0.15	6.66	0.0225	83.1	1.057	0.187
	0.02	50.00	0.0004	270.1	1.017	0.428
	0.04	25.00	0.0016	180.2	1.026	0.321
	0.06	16.66	0.0036	142.6	1.033	0.271
313	0.08	12.50	0.0064	119.2	1.039	0.243
	0.1	10.00	0.01	103.7	1.045	0.224
	0.12	8.33	0.0144	92.2	1.051	0.210
	0.15	6.66	0.0225	79.9	1.059	0.195

Table 3.11.a

$\bar{Q}$ VALUES OF BARIUM NITRATE IN METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURES.

Mass fraction of methanol Temperature (oK)	0%	10%	20%	30%
298	-581.8	-295.2	143.1	347.6
303	-382.6	231.8	255.1	343.7
308	-082.53	257.0	250.8	286.3
313	192.4	245.8	243.5	271.5

Table 3.11.b

$\bar{V}$ VALUES OF BARIUM NITRATE IN METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURES.

Mass fraction of methanol Temperature (oK)	0%	10%	20%	30%
298	0.0550	0.0542	0.0838	0.0863
303	0.0575	0.0690	0.980	0.0989
308	0.0727	0.0856	0.1236	0.1329
313	0.1039	0.1139	0.1478	0.1413

Table 3.12.a

M VALUES OF BARIUM NITRATE IN METHANOL-WATER SOLUTIONS AT

DIFFERENT TEMPERATURES.

Mass fraction of methanol Temperature (oK)	0%	10%	20%	30%
298	1.019	1.019	1.024	1.022
303	1.017	1.019	1.026	1.025
308	1.023	1.022	1.031	1.032
313	1.028	1.030	1.034	1.033

Table 3.12.b

K' VALUES OF BARIUM NITRATE IN METHANOL-WATER SOLUTIONS AT

DIFFERENT TEMPERATURES.

Mass fraction of methanol Temperature (oK)	0%	10%	20%	30%
298	1.61	1.19	1.47	1.16
303	1.69	1.19	1.25	1.25
308	1.53	1.31	1.32	1.06
313	1.5	1.30	1.37	1.11

Table 3.13

FREE ENERGY, ENERGY AND ENTROPY OF ACTIVATION FOR VISCOUS FLOW OF BARIUM NITRATE SOLUTION AT 298 $\overset{o}{K}$, (C=0.1 MOLE/L.)

Wt. % MeOH in MeOH-H_2O		$\triangle E^*$ K Cal	$\triangle F^*$ K Cal	$\triangle S^*$ K Cal ?
0%	solvent (water)	?.884	2.187	5.69
O·1 M	Ba$(NO_3)_2$	4.203	2.197	6.73
10%	solvent	4.243	2.371	6.28
	Ba$(NO_3)_2$	4.699	2.380	7.78
20%	solvent	4.691	2.520	7.29
	Ba$(NO_3)_2$	4.873	2.534	7.85
30%	solvent	4.967	2.619	7.88
	Ba$(NO_3)_2$	5.228	2.629	8.72

Table 3.14

TRANSPORT PROPERTIES OF VISCOUS FLOW OF BARIUM NITRATE IN

10% METHANOL-WATER SOLUTION AT 298 $^{\circ}$K.

Concentration (M) moles/lit	ΔE^* K.Cal.	ΔS^* e. u.	ΔF^* K Cal
0.02	4.703	7.826	2.372
0.04	4.705	7.818	2.375
0.06	4.705	7.815	2.376
0.08	4.704	7.802	2.378
0.1	4.699	7.781	2.380
0.12	4.702	7.785	2.382
0.15	4.690	7.734	2.385

How were these calculated from the formal experimental results? Can the thermodynamic quantities be experimentally determined with such an accuracy?

PLOTS OF $(n_r-1)/\sqrt{c}$ Vs $\sqrt{c}$ FOR BARIUM NITRATE IN DIFFERENT METHANOL—WATER COMPOSITIONS AT $298°K$.
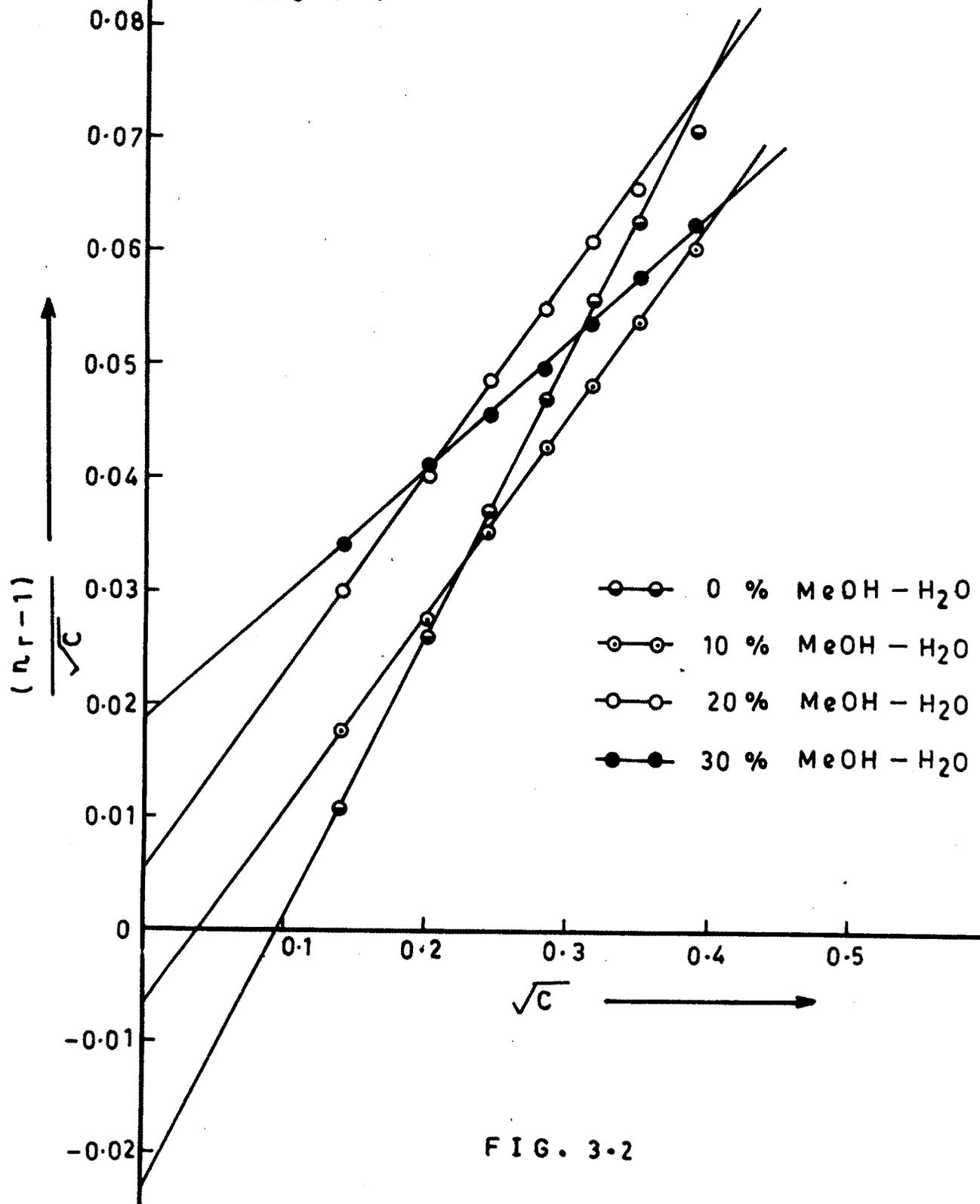
0 % MeOH — H_2O
10 % MeOH — H_2O
20 % MeOH — H_2O
30 % MeOH — H_2O

FIG. 3.2

PLOTS OF $(n_r-1)/\sqrt{C}$ Vs $\sqrt{C}$ FOR BARIUM NITRATE IN DIFFERENT METHANOL−WATER COMPOSITIONS AT 303° K .

Legend:
- 0 % MeOH − H_2O
- 10 % MeOH − H_2O
- 20 % MeOH − H_2O
- 30 % MeOH − H_2O

y-axis: $\dfrac{(n_r-1)}{\sqrt{C}}$

x-axis: $\sqrt{C}$

F I G . 3·3

PLOTS OF $(n_{r-1})/\sqrt{C}$ Vs $\sqrt{C}$ FOR BARIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 308°K.
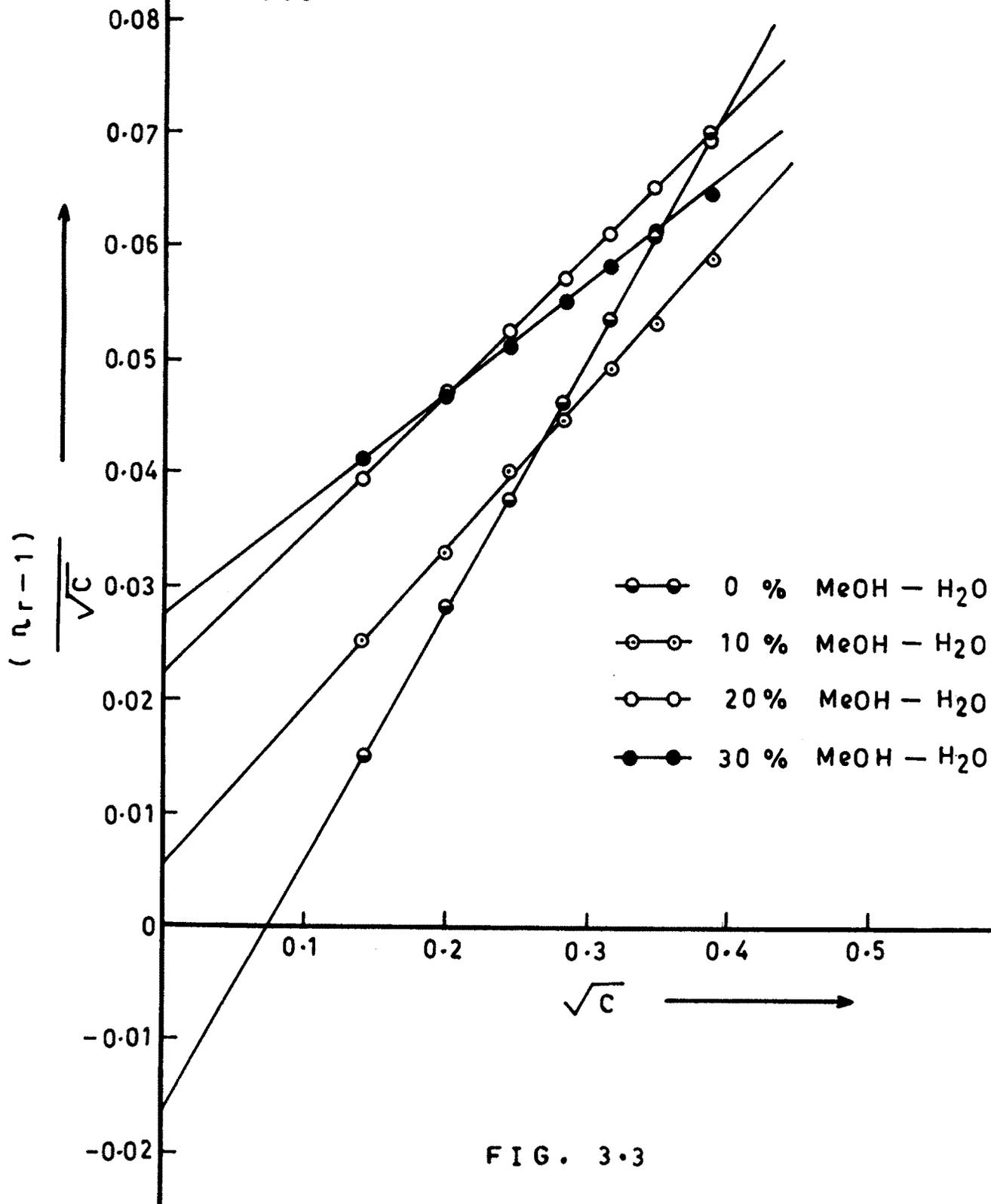
FIG. 3·4

PLOTS OF $(n_r-1)/\sqrt{C}$ vs $\sqrt{C}$ FOR BARIUM NITRATE IN DIFFERENT METHANOL–WATER COMPOSITIONS AT 313° K.
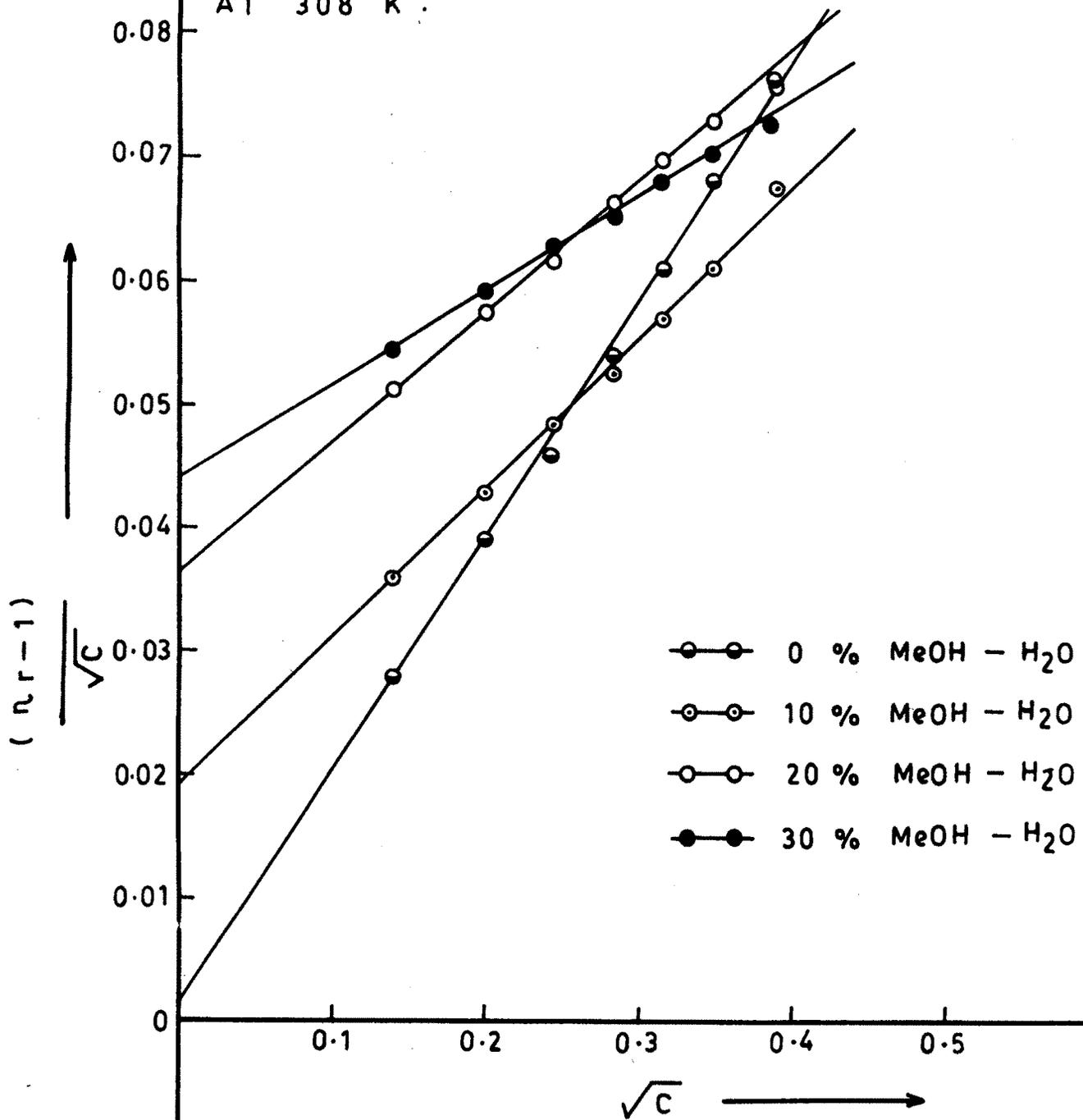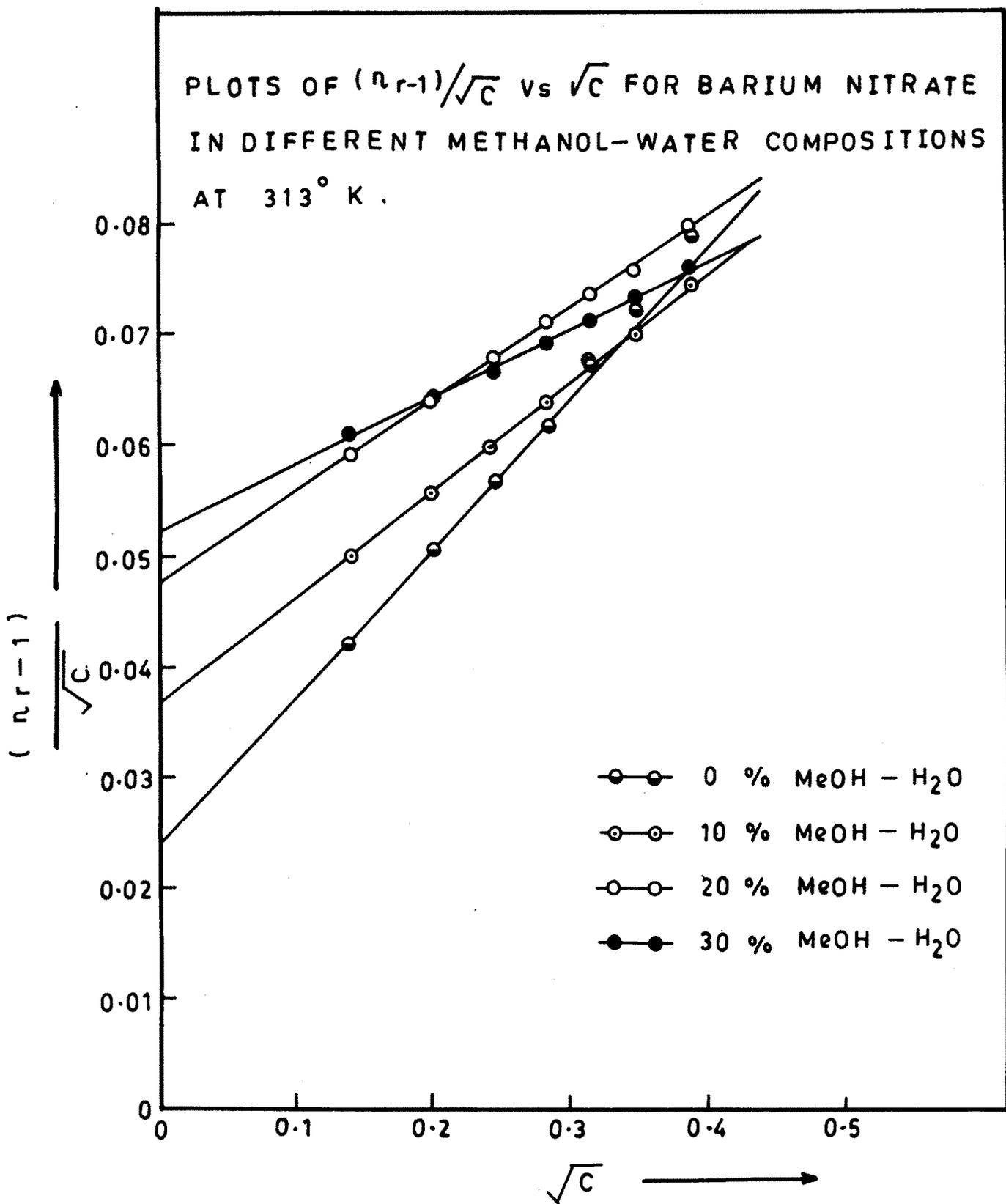
FIG. 3·5

PLOTS OF $\dfrac{1}{\text{Log } n_r}$ Vs $\dfrac{1}{C}$ FOR BARIUM NITRATE IN 0 % METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.

FIG. 3·6

PLOTS OF $\frac{1}{\log n_r}$ Vs $\frac{1}{C}$ FOR BARIUM NITRATE IN 10 % METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.

298° K
303° K
308° K
313° K

FIG. 3·7

PLOTS OF $\frac{1}{\text{Log } n_r}$ Vs $\frac{1}{C}$ FOR BARIUM NITRATE IN 20 % METHANOL–WATER SOLUTION AT DIFFERENT TEMPERATURES.

298° K
303° K
313° K
318° K

FIG. 3·8

PLOTS OF $\frac{1}{\log n_r}$ Vs $\frac{1}{C}$ FOR BARIUM NITRATE IN 30% METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.

○—● 298° K

⊙—⊙ 303° K

○—○ 313° K

●—● 318° K

FIG. 3·9

PLOTS OF η_r^2 Vs c^2 FOR BARIUM NITRATE IN 0 % METHANOL—WATER SOLUTION AT DIFFERENT TEMPERATURES.

298° K
303° K
308° K
313° K

η_r^2

c^2
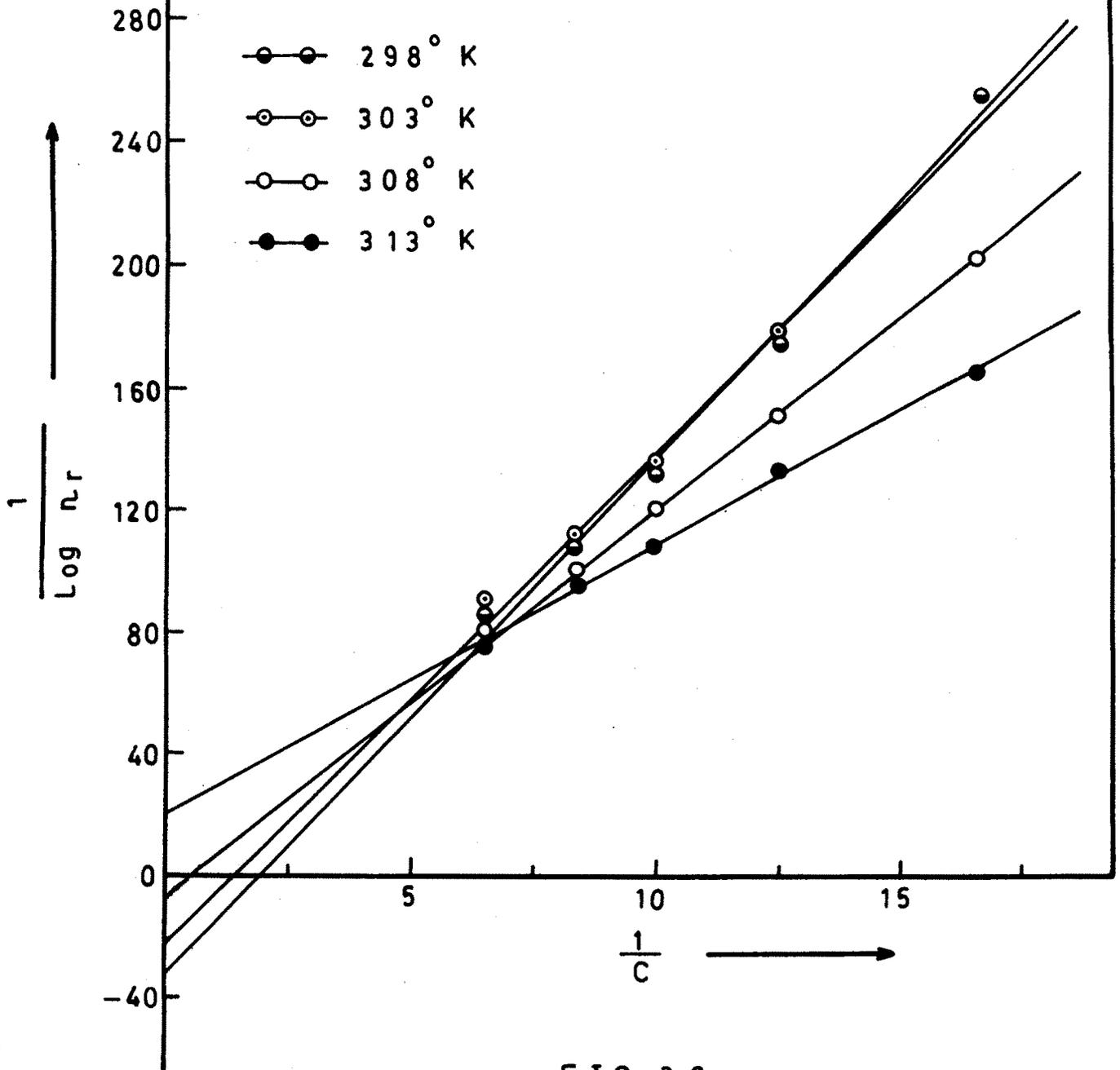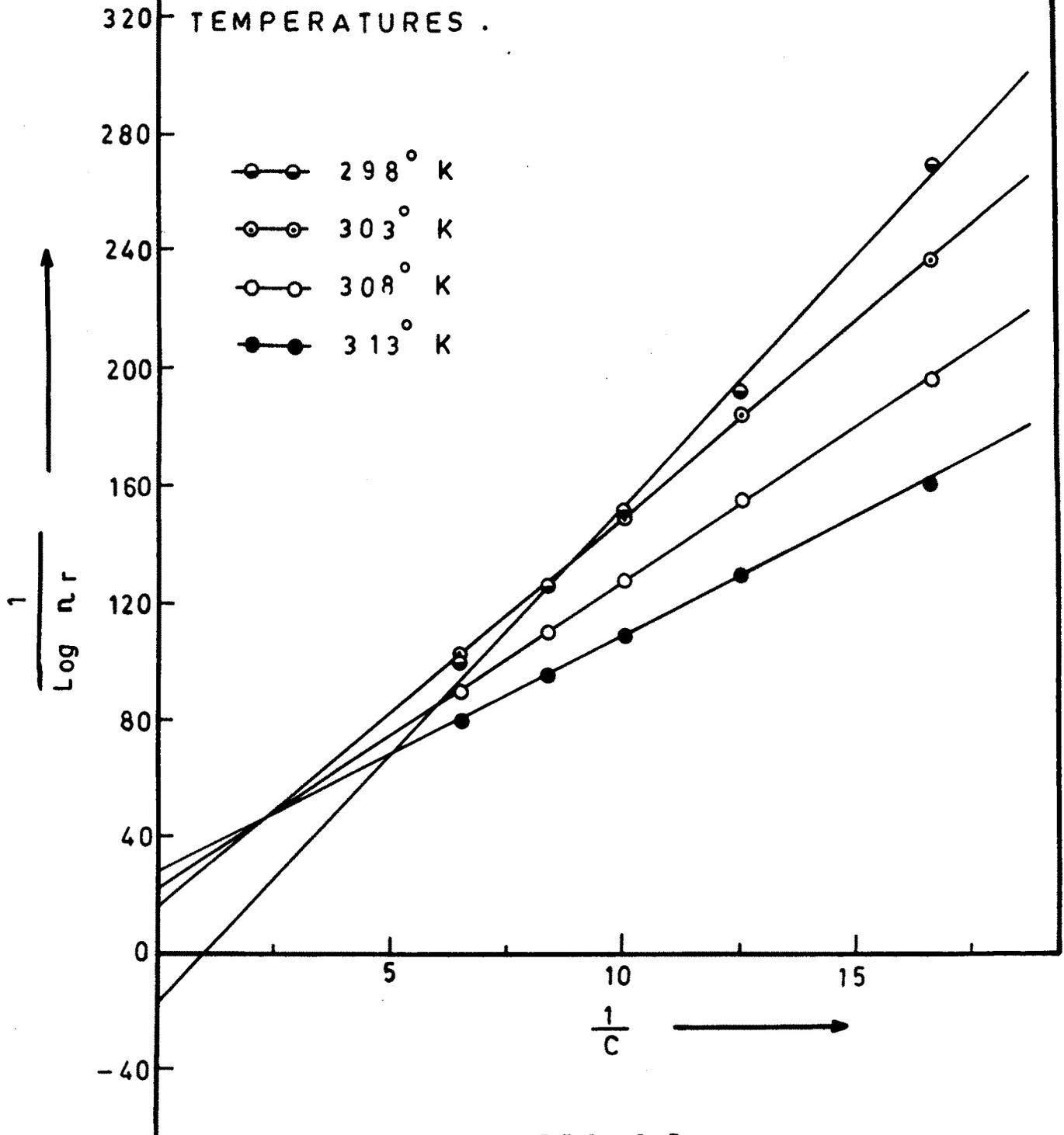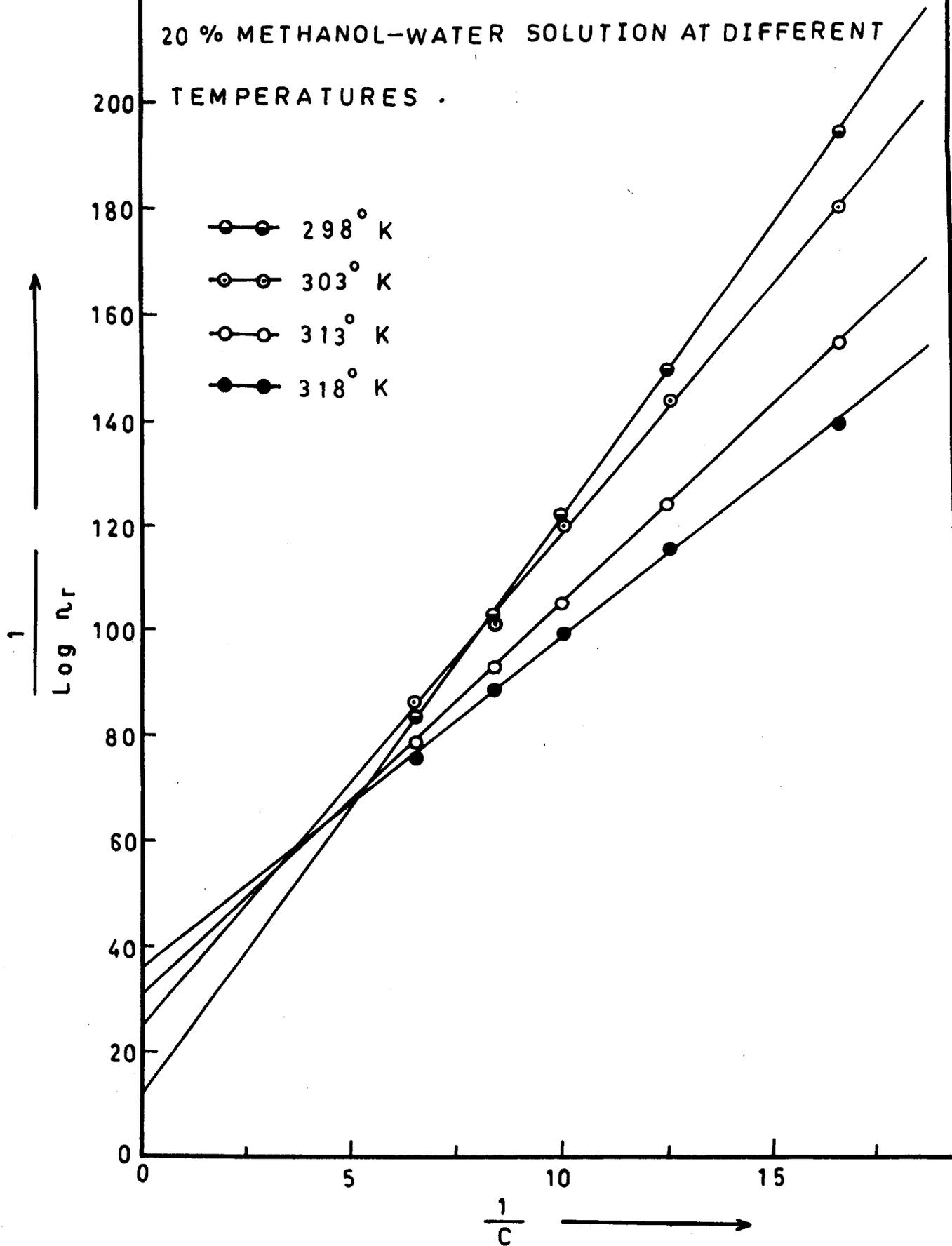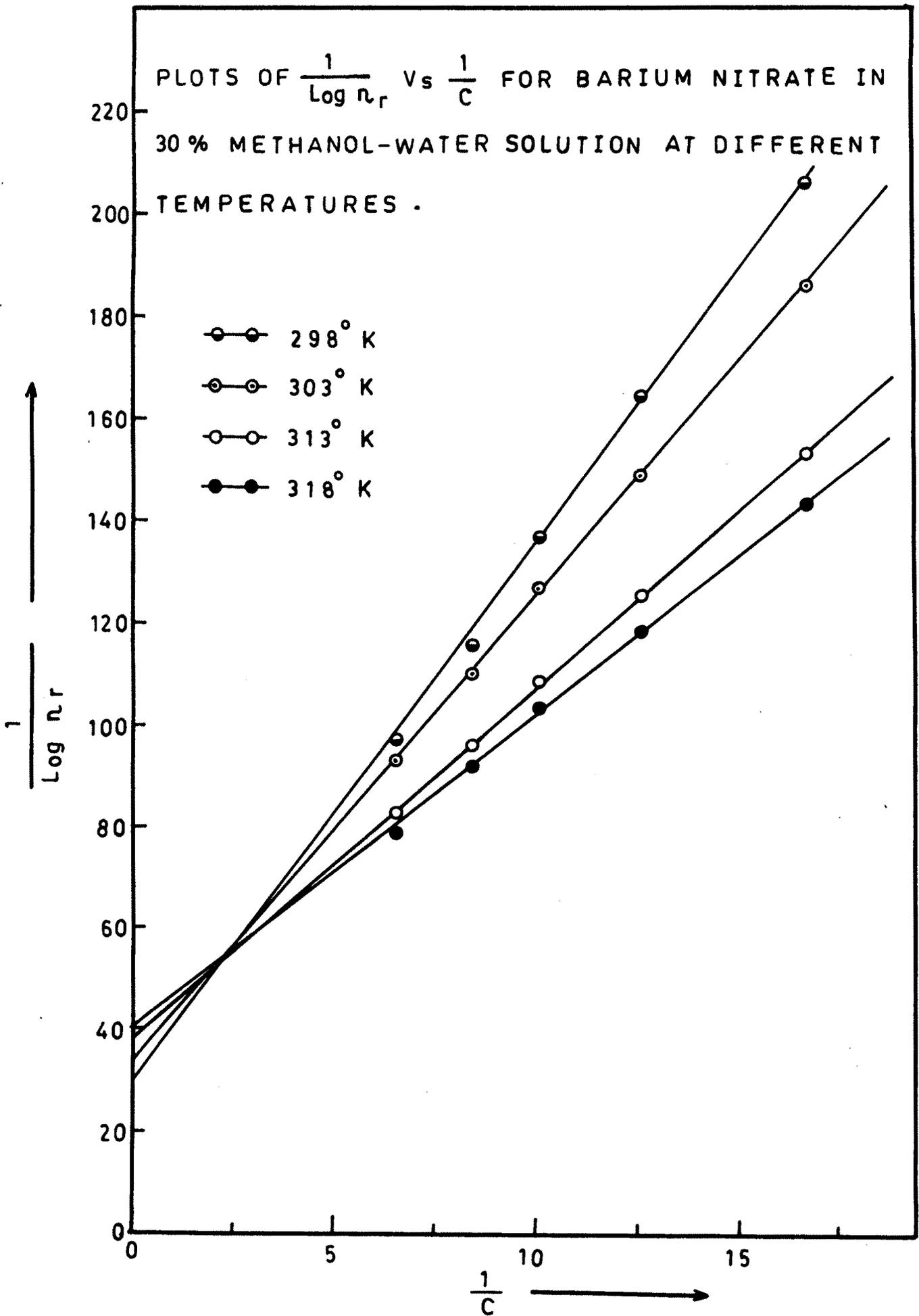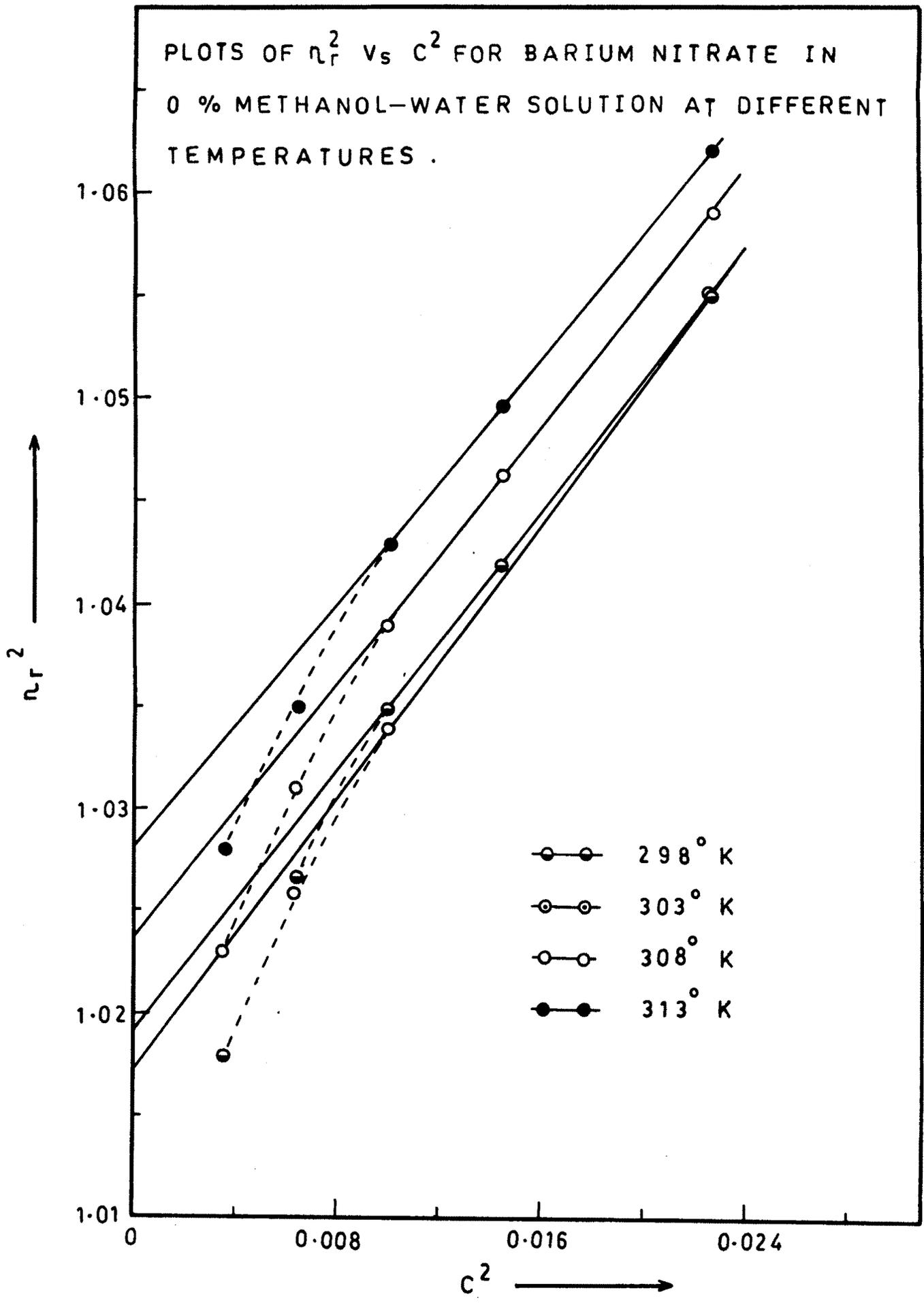
FIG. 3·10

PLOTS OF n_r^2 Vs C^2 FOR BARIUM NITRATE IN 10 % METHANOL—WATER SOLUTION AT DIFFERENT TEMPERATURES.

298° K
303° K
308° K
313° K

n_r^2

C^2
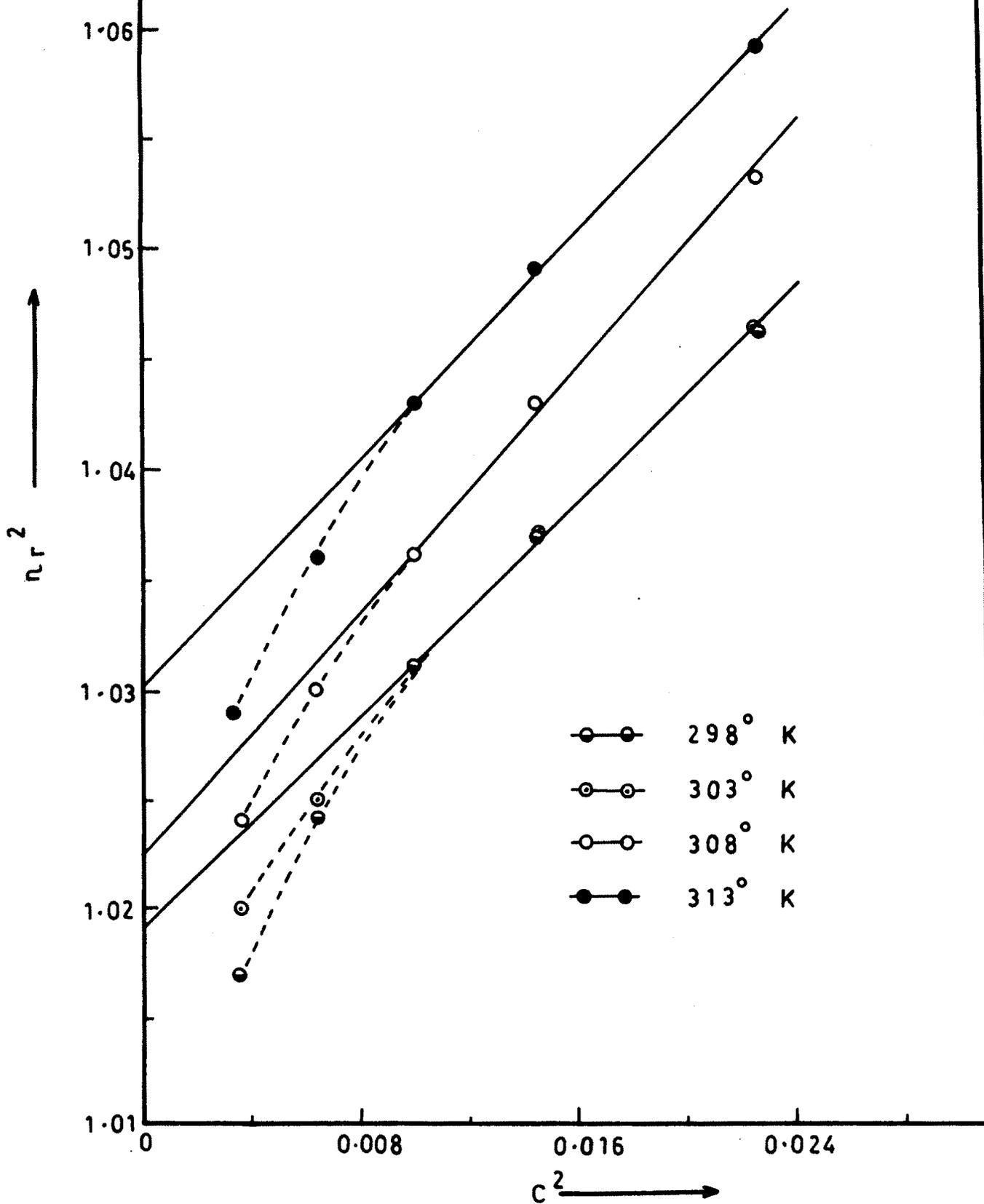
FIG. 3•11

PLOTS OF n_r^2 vs c^2 FOR BARIUM NITRATE IN 20% METHANOL—WATER SOLUTION AT DIFFERENT TEMPERATURES.

F I G. 3·12

PLOTS OF η_r^2 Vs C^2 FOR BARIUM NITRATE IN 30 % METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.

η_r^2 (y-axis)

C^2 (x-axis)

298° K
303° K
308° K
313° K
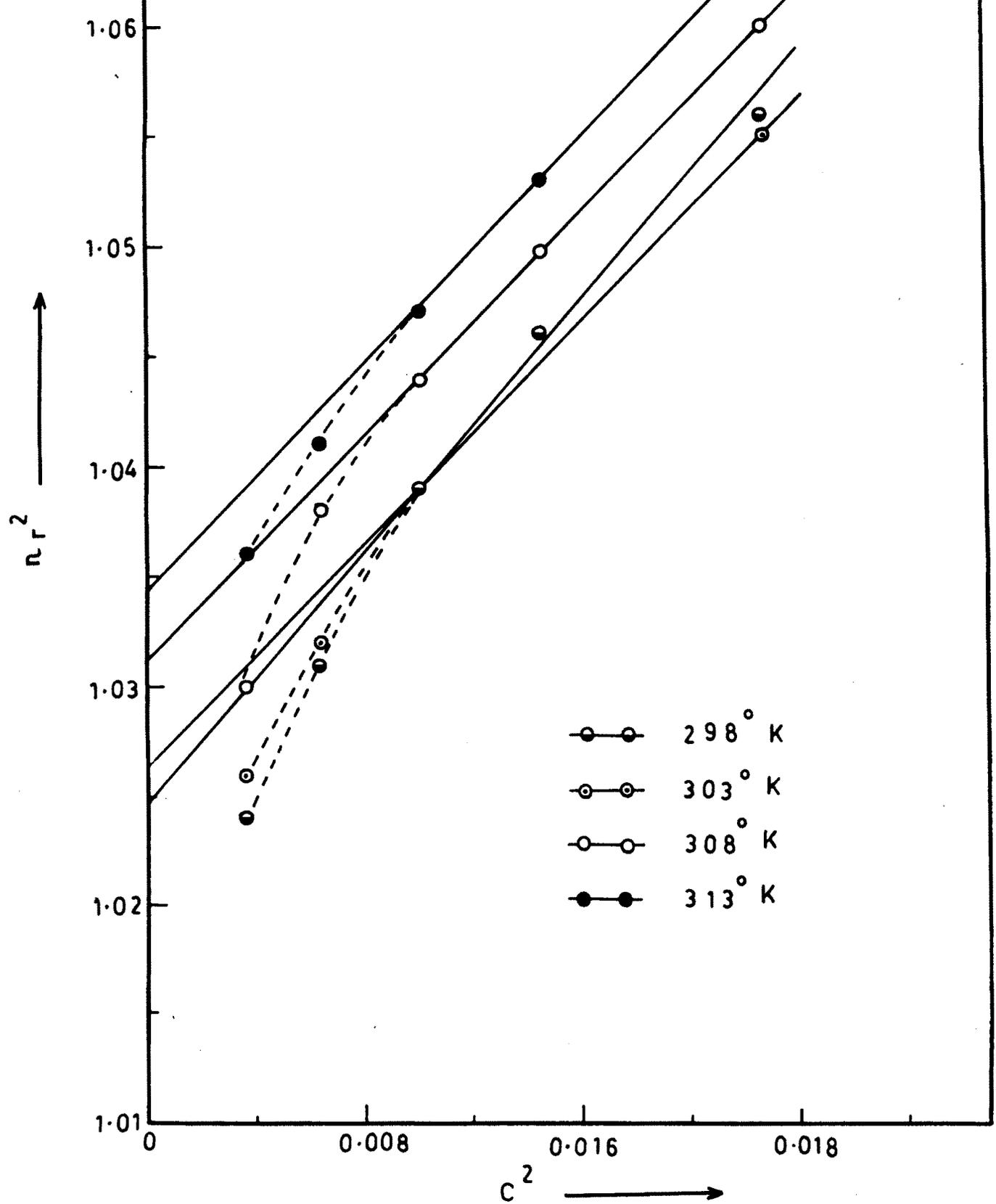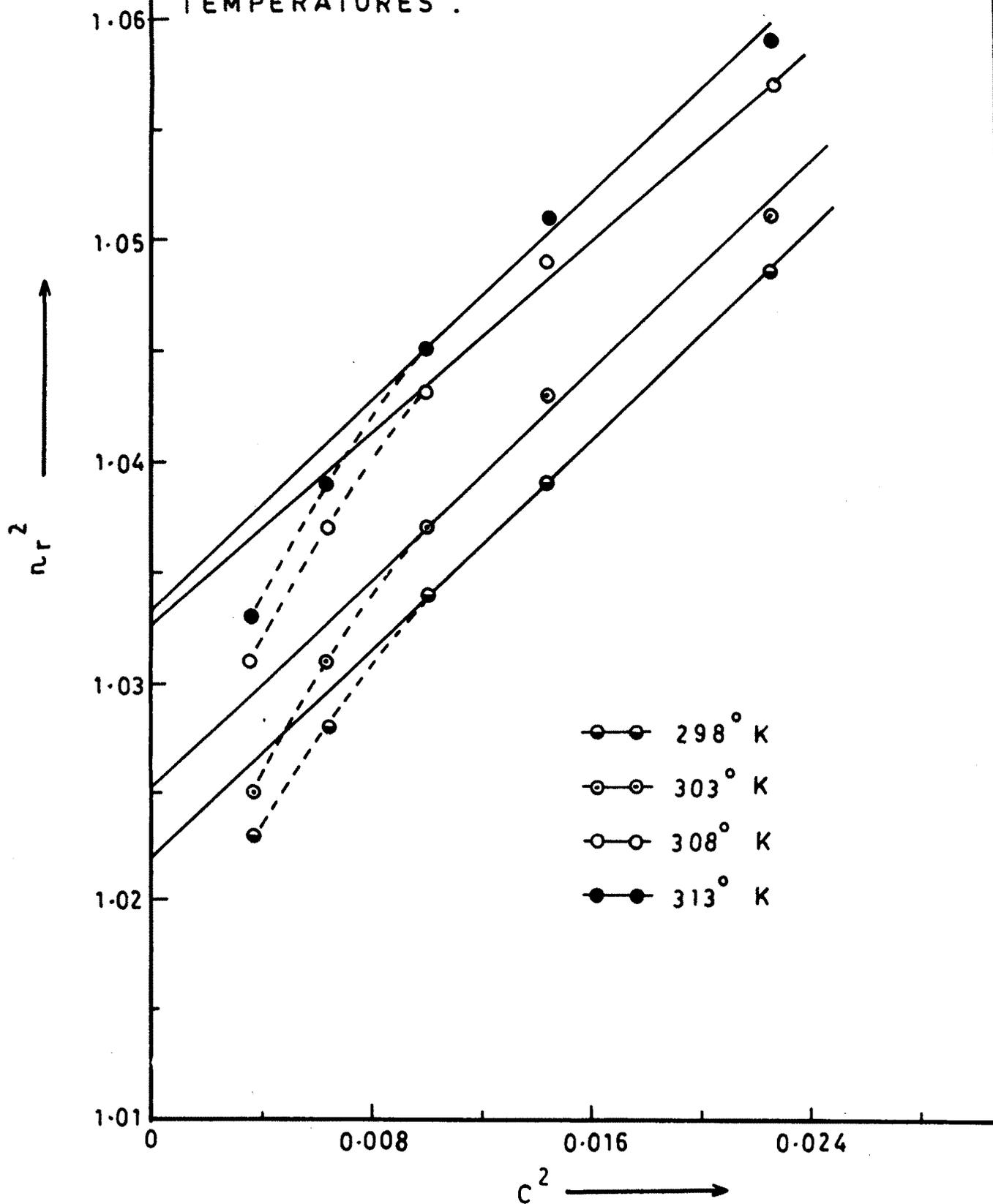
FIG. 3·13

PLOTS OF $\frac{n_{r-1}}{C}$ Vs C FOR BARIUM NITRATE IN 0 % METHANOL–WATER SOLUTION AT DIFFERENT TEMPERATURES.

○—● 298° K
○—⊙ 303° K
○—○ 308° K
●—● 313° K

FIG. 3·14

PLOTS OF $\frac{n_r - 1}{C}$ Vs C FOR BARIUM NITRATE IN 10 % METHANOL–WATER SOLUTION AT DIFFERENT TEMPERATURES.

298° K
303° K
308° K
313° K

FIG. 3·15

PLOTS OF $\frac{\eta r - 1}{C}$ Vs C FOR BARIUM NITRATE IN 20 % METHANOL−WATER SOLUTION AT DIFFERENT TEMPERATURES.

298° K
303° K
308° K
313° K

FIG. 3·16

PLOTS OF $\frac{\eta_r-1}{C}$ Vs C FOR BARIUM NITRATE IN 30 % METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.

298° K
303° K
308° K
313° K

F I G . 3·17