CHAPTER-IV

CALCIUM NITRATE IN METHANOL–WATER SYSTEM

(RESULTS AND DISCUSSION)

RESULTS AND DISCUSSION :

In chapter III, the results on the viscosity determination of $Ba(NO_3)_2$ solutions of different concentrations in different methanol compositions and at different temperatures have been presented and fully discussed on the basis of various equations. In this chapter the results on calcium nitrate solutions of different concentrations, different methanol compositions and different temperature will be described and discussed on a similar line.

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

i] Effect of concentration of calcium nitrate on viscosity.

ii] Effect of methyl alcohol % on viscosity.

iii] Effect of temperature on viscosity.

iv] The transport properties.

4.1 EFFECT OF CONCENTRATION OF CALCIUM NITRATE ON VISCO SITY

The results on the effect of variation of calcium nitrate concentration (0.02 - 0.15 molar) in methanol-water ($MeOH-H_2O$) solutions (0%, 10%, 20%, 30% MeOH W/W) at 298° K are given in Table 4.1. From Table 4.1 it has been noticed that as the concentration of calcium nitrate increases the viscosity (η), and the relative viscosity (ηr) increases; but the fluidity (ϕ), the reciprocal of viscosity decreases. The similar results were obtained for Barium nitrate. For calcium nitrate-water solutions (0% methanol) at 298 ^{o}K, the viscosity (η) increases from 0.89395 to 0.9358, the relative viscosity (ηr) increases from 1.00410 to 1.05112 and the fluidity (ϕ) decreases from 1.11863 to 1.06859.

Similar results were obtained for calcium nitrate in methanol-water ($MeOH-H_2O$) solution at 303^{o}, 308^{o} and 313^{o}K temperatures. (Table Nos. 4.2 - 4.4).

4.2 EFFECT OF METHYL ALCOHOL ON VISCOSITY :

At a given temperature (298 ^{o}K) and for a certain concentration of calcium nitrate (0.06 M) the viscosity (η) and relative viscosity (ηr) increase as the proportion of methyl alcohol (10%, 20%, 30% $MeOH-H_2O$, w/w) increases, but the fluidity (ϕ) decreases (Table 4.1). The similar effect of methyl alcohol on viscosity of Barium nitrate solution was observed.

4.3 EFFECT OF TEMPERATURE ON VISCOSITY :

The effect of temperature on viscosity of calcium nitrate solutions is similar to that of Barium nitrate. The data is recorded in Table Nos. 4.1-4.4. It indicates that the viscosity (η) and relative viscosity (ηr) of calcium nitrate in methanol-water solutions decrease as the temperature increases but the fluidity (ϕ) increases with temperature.

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

i) Jones-Dole Equation

ii) Vand Equation

iii) Moulik Equation

iv) Thomas Equation

4.4.1] JONES-DOLE EQUATION

The experimental data (Table Nos. 4.1-4.4) of Calcium nitrate is analyzed in the light of Jones-Dole equation[76]. The Jones-Dole equation is found to be valid in the concentration range 0.02-0.15 M as the plots of $\eta_r - 1 / \sqrt{C}$ Vs $\sqrt{C}$ are linear as shown in Fig. 4.1-4.4, similar to that of Barium nitrate. The values of A and B calculated by employing both graphical and least square method are given in Tables 4.5 and 4.6 respectively.

a) 'A' VALUES

It can be seen from Table 4.5 that the values of 'A' coefficient are very small and even negative. It indicates very weak ion-ion or solute-solute interaction[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. Similar trend is obtained in case of A values of Barium nitrate.

A values of Calcium nitrate and Barium nitrate are identical in water. But in methanol soluions, A values of calcium nitrate are higher than those of Barium nitrate for the same temperature and methanol concentration. Ionic radii[89] of Calcium is 0.99 Å and that of Barium is 1.35 Å. Ionic radius of calcium is less than that of Barium whereas A values of calcium nitrate are higher than those of Barium nitrate. Therefore it may be concluded that the ion-ion interaction should be of the order $Ca^{++} > Ba^{++}$.

This is in agreement with the results of D.K. Dash, P.B. Das[37] and N.C. Das, P.B. Das[35]. According to D.K. Dash and P.B. Das the A values of Cadmium nitrate and Strontium nitrate in 10% methanol solution at 303 °K are 10.4 and 9.3 respectively whereas ionic radius of Cadmium is less than that of Strontium. N.C. Das and P.B. Das has given A values for sodium nitrate and potassium nitrate in 10% dioxane solutions at 303 °K are 7.0 and 6.3 respectively and here also we see that ionic radius of sodium is less than that of potassium.

b) <u>'B' VALUES</u> :

It is seen from Table 4.6 that B values are all positive but small in magnitude and decrease with increase in temperature and methanol content at a particular temperature. The trend in B values of calcium nitrate is similar to that of Barium nitrate. However B values of Calcium nitrate seem to be higher than those of Barium nitrate at the same temperature and methanol concentration.

It has been shown[90] that the B coefficient may be considered as being formed by two contributions, one positive and one negative. The former comes from the tendency of the ions to attract the solvent molecules around it centro-symmetrically, while the latter stems from the fact that the structure of the solvent itself goes against this tendency, so that these two oppositing influences can cause breakdown in the solvent structure beyond the first solvent shell.

Generally, the positive contribution prevails over the negative one. Producing an increase in the viscosity of the solution with respect to that of the solvent. Only for solvents with extended three-dimensional structure, due to hydrogen bonds[75,91] does the negative contribution dominate for ions with low charge density, with negative B-values and a relative decrease in the viscosity of the solution with respect to that of the solvent can be found. Following the above lines, one can discuss the variation of B coefficients in terms of viscosity effects. In our results the charge density decreases in the order Ca^{++} to Ba^{++} and one can expect that B-values vary in the order $Ca(NO_3)_2$ > $Ba(NO_3)_2$.

C) DEPENDENCE OF 'B' ON TEMPERATURE :

The 'B' coefficients of Calcium nitrate and Barium nitrate decrease with increase in temperature. This indicates[75] that there is significant decrease in η_A. However in spite of this decrease the sum of $\eta_E + \eta_A$ will be still larger than η_D and B is positive. The 'B' value is found to be of the order $Ca^{++} > Ba^{++}$. The lesser the value of 'B' the greater is the ion-solvent interaction. So the ion-solvent interaction is of the order $Ba^{++} > Ca^{++}$.

The value dB/dT for Calcium nitrate in 0, 10, 20 and 30

% methanol-water is negative and suggests[74] that Calcium nitrate also behaves as a structure maker/promoter.

d) <u>DEPENDENCE OF 'B' ON METHANOL CONTENT</u> :

The value of 'B' coefficient for calcium nitrate decrease with increase in methanol content in the solvent mixture (Table 4.6). These results are similar to that of Barium nitrate. This 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]. 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.

e) <u>DEPENDENCE OF 'B' ON CATION</u>

Ions with greater crystal radii and small surface charge density, Ba^{++}, would have a weak orienting effect in the first layer. Therefore η_E and η_A will be small. Also, there exists a considerable amount of distortion in the vicinity of such ions due to the competition between the ionic field and bulk structure and consequently η_D will be large. Thus 'B' will be smaller for Ba^{++} salt than for Ca^{++} salt (Table Nos. 3.6 and 4.6). So the order of ion-solvent interaction should be $Ba^{++} > Ca^{++}$.

4.4.2 <u>VAND EQUATION</u> :

The viscosity data of Calcium nitrate have been examined in the light of Vand[54] equation. Similar to Barium nitrate Vand equation is also applicable for Calcium nitrate in the concentration range 0.06 - 0.15 M. $\frac{1}{\log \eta_r}$ is plotted against $\frac{1}{C}$ by using data given in Table Nos. 4.7-4.10. The plots of $\frac{1}{\log \eta_r}$ Vs $\frac{1}{C}$ are shown in Figs. 4.5-4.8. The viscosity parameters Q and $\bar{V}$ are presented in Table Nos. 4.11.a and 4.11.b respectively. It is seen that molar volume ($\bar{V}$) and the interaction coefficient (Q) both increase with temperature and methanol concentrations. 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 cosphere of the ions due to thermal agitation. On the basis of the increase in the value of $\bar{V}$ of Calcium nitrate in methanol solutions, it can be inferred that the ions get more and more hydrated in the presence of methanol.

From Table Nos. 3.11.a, 3.11.b and 4.11.a, 4.11.b it has been noticed that the viscosity parameters both Q and $\bar{V}$ of Calcium nitrate are higher than that of Barium nitrate for the same temperature and methanol concentration.

From Table No. 4.15 it suppports the idea[84,85] that both Ca^{++} and Ba^{++} are electrostrictive structure-making ions with positive ionic volumes, hydration numbers and entropy changes.

4.4.3 <u>MOULIK</u> <u>EQUATION</u>

Moulik equation is not valid for Calcium nitrate below 0.1 M concentration. η_r^2 is plotted against C^2 by applying data given in Table 4.7-4.10. Plots of η_r^2 Vs C^2 are shown in Figs. 4.9-4.12. Viscosity parameters M and

K' are recorded in Table No. 4.12.a and 4.12.b respectively. Similar to that of Barium nitrate the constant M increases with increase in temperature and concentration of methyl alcohol. The constant K' decreass with increase in temperature and concentration of methyl alcohol.

From Table Nos. 3.12.a, 3.12.b and 4.12.a, 4.12.b it is seen that the viscosity parameters M and K' of Calcium nitrate are higher than those of Barium nitrate for the same temperature and methanol concentration.

4.4.4 THOMAS EQUATION :

Thomas equation is not valid for Calcium nitrate in methanol solutions in the concentration range C.02 - 0.15 M. $\frac{\eta_r - 1}{C}$ is plotted against C by using data given in Table Nos. 4.7-4.10. Plots of $\frac{\eta_r - 1}{C}$ Vs C shown in Fig. 4.13-4.16 are not linaear.

4.5 THE TRANSPORT PROPERTIES (ACTIVATION PARAMETERS)

Proceeding along similar lines of Eyring[55] and Nightingale[62] we have calculated energy of activation (ΔE^*), the free energy of activation (ΔF^*), and entropy of activation (ΔS^*) for the solvents and for Calcium nitrate (C = 0.1 MOLE/L) in different wt. % of methanol at 298 ^{o}K. The results are given in Table 4.13.

From results it is evident that energy and entropy of activation of the viscous flow of solution are higher than those of solvents. It indicates little solute-solvent interaction[27,28,30]. It also clearly indicates the structure making effect[37] of Calcium nitrate.

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

The thermodynamic parameters of viscous flow of Calcium nitrate in 10% methanol-water solution are calulated[55] at 298 ^{o}K. The values are given in Table 4.14. From Table 4.14 it is seen that ΔE^* of viscous flow remains constant with an increase in concentration of Calcium nitrare, ΔS^* decreases and ΔF^* increases slightly. It clearly indicates[88] that Calcium nitrate is structure making.

Comparision of the data (Table Nos. 3.13 and 4.13) for the activation energy of viscous flow for Barium nitrate and Calcium nitrate clearly indicates that Calcium ion requires less activation energy than that of Barium ion. The increase is less in the case of Ca^{++} and more in the case of Ba^{++}.

CONCLUSION

In the present investigations, studies on viscosity of Barium nitrate and Calcium nitrate solutions in methanol-water system have been reported. Viscosity data for Barium nitrate and Calcium nitrate in methanol-water ($MeOH-H_2O$) solutions (0%, 10%, 20% and 30% MeOH, W/W) at 298^{o}, 303^{o}, 308^{o} and 313^{o} K are reported.

The experimental results of viscosity have been analyzed using the Jones-Dole equation, Vand equation, Moulik equation and Thomas equation. Jones-Dole equation is valid for both electrolytes in cencentration range 0.02 - 0.15 M. Vand equation is applicable for both electrolytes in the concentration range 0.06 - 0.15 M. Moulik equation is not valid for Barium nitrate and Calcium nitrate below 0.1 M concentration. Thomas equation is invalid for both electrolytes in the concentration range 0.02 - 0.15 M. The value of dB/dT for both electrolytes is negative and therefore Barium nitrate and Calcium nitrate behaves as structure makers/promoters. Both Ba^{++} and Ca^{++} are electrostrictive structure-making ions with positive ionic volumes ($\overline{V} \pm$) and hydration numbers (NB).

From the study of transport properties of both electrolytes we conclude that there is little solute-solvent interaction due to structure-making effect of electrolytes. Ba^{++} and Ca^{++} associates with the solvent molecule in the co-sphere and stabilises the solvent structure. They predominates over the structure-breaking properties of their partner.

From the comparision between A values of Barium nitrate and Calcium nitrate solution it is concluded that ion-ion interaction is found to be more for Ca^{++} than Ba^{++} ions. `B'values for Calcium nitrate solutions are found to be nearly double the values for Barium nitrate. This has been explained on the basis of the difference in ionic radii of

Ca^{++} and Ba^{++} ions indicating that ion-solvent interaction should be more for Ba^{++}. From the study of transport properties of both electrolytes it is clear in general that ΔE^{*}, ΔS^{*} and ΔF^{*} values are more for Ba^{++} ion than those of Ca^{++} ion.

Table 4.1

VISCOSITY DATA FOR CALCIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 298 ^{o}K.

concentration moles/lit	$(\text{Conc}^n)^{1/2}$	η $mNSm^{-2}$	η_r	ϕ	$\frac{\eta_r - 1}{\sqrt{C}}$
Wt. % MeOH in MeOH-H_2O = 0					
0.02	0.1414	0.89395	1.00410	1.11863	0.029
0.04	0.2	0.89991	1.01080	1.11121	0.054
0.06	0.2449	0.90577	1.01738	1.10402	0.071
0.08	0.2828	0.91220	1.02460	1.09624	0.087
0.1	0.3162	0.91928	1.03256	1.08779	0.103
0.12	0.3464	0.92514	1.03914	1.08091	0.113
0.15	0.3873	0.93581	1.05112	1.06859	0.132
Wt. % MeOH in MeOH-H_2O = 10					
0.02	0.1414	1.15297	1.00593	0.86732	0.042
0.04	0.2	1.15972	1.01182	0.86227	0.059
0.06	0.2449	1.16610	1.01738	0.85755	0.071
0.08	0.2828	1.17308	1.02347	0.85245	0.083
0.1	0.3162	1.17952	1.02909	0.84780	0.092
0.12	0.3464	1.18627	1.03498	0.84297	0.101
0.15	0.3873	1.19721	1.04453	0.83526	0.115
Wt. % MeOH in MeOH-H_2O = 20					
0.02	0.1414	1.39442	1.00805	0.71693	0.057
0.04	0.2	1.40393	1.01463	0.71228	0.073

0.06	0.2449	1.41248	1.02081	0.70797	0.085
0.08	0.2828	1.42085	1.02686	0.70380	0.095
0.1	0.3162	1.42874	1.03256	0.69991	0.103
0.12	0.3464	1.43689	1.03845	0.69594	0.111
0.15	0.3873	1.44959	1.04763	0.68984	0.123

Wt. % MeOH in MeOH-H_2O = 30

0.02	0.1414	1.54575	1.00904	0.64693	0.064
0.04	0.2	1.55588	1.01565	0.64272	0.078
0.06	0.2449	1.56492	1.02155	0.63901	0.088
0.08	0.2828	1.57393	1.02743	0.63535	0.097
0.1	0.3162	1.58227	1.03288	0.63199	0.104
0.12	0.3464	1.59133	1.03879	0.62840	0.112
0.15	0.3873	1.60369	1.04686	0.62355	0.121

Table 4.2

VISCOSITY DATA FOR CALCIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 303 ^{o}K.

concentration moles/lit	$(conc^{n})^{1/2}$	η $mNsm^{-2}$	η_r	ϕ	$\frac{\eta_r - 1}{\sqrt{c}}$
Wt. % MeOH in MeOH-H_2O = 0					
0.02	0.1414	0.80201	1.00565	1.24687	0.04
0.04	0.2	0.80742	1.01244	1.23851	0.062
0.06	0.2449	0.81292	1.01934	1.23012	0.079
0.08	0.2828	0.81892	1.02686	1.22112	0.095
0.1	0.3162	0.82422	1.03351	1.21326	0.106
0.12	0.3464	0.83009	1.04087	1.20468	0.118
0.15	0.3873	0.93649	1.05189	1.06780	0.134
Wt. % MeOH in MeOH-H_2O = 10					
0.02	0.1414	1.02424	1.00735	0.97633	0.052
0.04	0.2	1.03063	1.01364	0.97027	0.068
0.06	0.2449	1.03693	1.01983	0.96438	0.081
0.08	0.2828	1.04293	1.02573	0.95883	0.091
0.1	0.3162	1.04892	1.03162	0.95336	0.1
0.12	0.3464	1.05515	1.03775	0.94772	0.109
0.15	0.3873	1.06362	1.04608	0.94018	0.119
Wt. % MeOH in MeOH-H_2O = 20					
0.02	0.1414	1.21852	1.00975	0.82066	0.069
0.04	0.2	1.22706	1.01683	0.81494	0.084

0.06	0.2449	1.23453	1.02302	0.81001	0.094
0.08	0.2828	1.24258	1.02969	0.80477	0.105
0.1	0.3162	1.24949	1.03541	0.80032	0.112
0.12	0.3464	1.25650	1.04122	0.79585	0.119
0.15	0.3873	1.26750	1.05034	0.78894	0.13
Wt. % MeOH in MeOH-H_2O = 30					
0.02	0.1414	1.33053	1.01102	0.75157	0.078
0.04	0.2	1.33974	1.01802	0.74641	0.09
0.06	0.2449	1.34761	1.02400	0.74205	0.098
0.08	0.2828	1.35622	1.03054	0.73734	0.108
0.1	0.3162	1.36263	1.03541	0.73387	0.112
0.12	0.3464	1.37027	1.04122	0.72977	0.119
0.15	0.3873	1.38023	1.04879	0.72451	0.126

Table 4.3

VISCOSITY DATA FOR CALCIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 308 ^{o}K.

concentration moles/lit	$(conc^{n})^{1/2}$	η $mNSm^{-2}$	η_r	ϕ	$\frac{\eta_r - 1}{\sqrt{C}}$
Wt. % MeOH in MeOH-H_2O = 0					
0.02	0.1414	0.72458	1.00721	1.38010	0.051
0.04	0.2	0.73009	1.01486	1.36969	0.074
0.06	0.2449	0.73525	1.02204	1.36007	0.09
0.08	0.2828	0.74034	1.02912	1.35071	0.103
0.1	0.3162	0.74555	1.03636	1.34127	0.115
0.12	0.3464	0.75055	1.04330	1.33235	0.125
0.15	0.3873	0.75812	1.05383	1.31904	0.139
Wt. % MeOH in MeOH-H_2O = 10					
0.02	0.1414	0.90635	1.00862	1.10331	0.061
0.04	0.2	0.91230	1.01524	1.09612	0.076
0.06	0.2449	0.91775	1.02130	1.08961	0.087
0.08	0.2828	0.92326	1.02743	1.08311	0.097
0. 1	0.3162	0.92844	1.03320	1.07706	0.105
0.12	0.3464	0.93409	1.03948	1.07056	0.114
0.15	0.3873	0.94176	1.04802	1.06183	0.124
Wt. % MeOH in MeOH-H_2O = 20					
0.02	0.1414	1.07267	1.01088	0.93224	0.077
0.04	0.2	1.08047	1.01823	0.92552	0.091

0.06	0.2449	1.08737	1.02473	0.91964	0.101
0.08	0.2828	1.09413	1.03110	0.91396	0.11
0.1	0.3162	1.1007	1.03731	0.90849	0.118
0.12	0.3464	1.10716	1.04338	0.90321	0.125
0.15	0.3873	1.11619	1.05189	0.89590	0.134

Wt. % MeOH in MeOH-H_2O = 30

0.02	0.1414	1.16680	1.01244	0.85703	0.088
0.04	0.2	1.17513	1.01967	0.85096	0.098
0.06	0.2449	1.18237	1.02545	0.84575	0.106
0.08	0.2828	1.18961	1.03223	0.84061	0.114
0.1	0.3162	1.19582	1.03762	0.83624	0.119
0.12	0.3464	1.20242	1.04335	0.83164	0.125
0.15	0.3873	1.21138	1.05112	0.82550	0.132

Table 4.4

VISCOSITY DATA FOR CALCIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 318 ^{o}K.

concentration moles/lit	$(conc^{n})^{1/2}$	η $mNsm^{-2}$	η_r	ϕ	$\frac{\eta_r - 1}{\sqrt{c}}$
Wt. % MeOH in MeOH-H_2O = 0					
0.02	0.1414	0.65918	1.00932	1.51702	0.066
0.04	0.2	0.66450	1.01746	1.50488	0.087
0.06	0.2449	0.66925	1.02473	1.49420	0.101
0.08	0.2828	0.67433	1.03252	1.48293	0.115
0.1	0.3162	0.67911	1.03984	1.47249	0.126
0.12	0.3464	0.68386	1.04711	1.46227	0.136
0.15	0.3873	0.69103	1.05809	1.44709	0.15
Wt. % MeOH in MeOH-H_2O = 10					
0.02	0.1414	0.81034	1.00975	1.23403	0.069
0.04	0.2	0.81591	1.01668	1.22562	0.083
0.06	0.2449	0.82099	1.02302	1.21802	0.094
0.08	0.2828	0.82590	1.02913	1.21079	0.103
0.1	0.3162	0.83069	1.03510	1.20381	0.111
0.12	0.3464	0.83533	1.04088	1.19712	0.118
0.15	0.3873	0.84231	1.04957	1.18721	0.128
Wt. % MeOH in MeOH-H_2O = 20					
0.02	0.1414	0.95201	1.01145	1.05041	0.081
0.04	0.2	0.95895	1.01883	1.04281	0.094

0.06	0.2449	0.96496	1.02522	1.03630	0.103
0.08	0.2828	0.97077	1.03139	1.03011	0.111
0.1	0.3162	0.97575	1.03668	1.02485	0.116
0.12	0.3464	0.98165	1.04295	1.01869	0.124
0.15	0.3873	0.98934	1.05112	1.01077	0.132
Wt. % MeOH in MeOH-H_2O = 30					
0.02	0.1414	1.02801	1.01287	0.97275	0.091
0.04	0.2	1.03630	1.02104	0.96496	0.1
0.06	0.2449	1.04154	1.02620	0.96012	0.107
0.08	0.2828	1.04738	1.03196	0.95476	0.113
0.1	0.3162	1.05249	1.03699	0.95012	0.117
0.12	0.3464	1.05784	1.04226	0.94532	0.122
0.15	0.3873	1.06478	1.04957	0.93915	0.128

Table 4.5 $A.10^{3}/l^{1/2}\ mol^{-1/2}$

Mass fraction of methanol / Temperature (oK)	0%	10%	20%	30%
298	-0.029 (-0.030)	0.002 (0.001)	0.02 (0.019)	0.032 (0.031)
303	-0.014 (-0.014)	0.013 (0.013)	0.035 (0.034)	0.051 (0.049)
308	0.002 (0.002)	0.025 (0.025)	0.045 (0.044)	0.063 (0.062)
313	0.019 (0.017)	0.036 (0.035)	0.053 (0.053)	0.07 (0.069)

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

Table 4.6 $B/l\ mol^{-1}$

Mass fraction of methanol / Temperature (K)	0%	10%	20%	30%
298	0.43 (0.417)	0.286 (0.286)	0.265 (0.264)	0.233 (0.229)
303	0.385 (0.381)	0.274 (0.275)	0.243 (0.247)	0.188 (0.199)
308	0.366 (0.364)	0.258 (0.252)	0.232 (0.233)	0.182 (0.180)
313	0.340 (0.342)	0.275 (0.241)	0.206 (0.202)	0.151 (0.150)

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

Table 4.7

VISCOSITY DATA FOR CALCIUM NITRATE IN 0% METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURES.

Temperature (oK)	concentration (C) moles/lit	$\frac{1}{C}$	C^2	$\frac{1}{\log \eta_r}$	η_r^2	η_r-1/C
	0.02	50.00	0.0004	562.7	1.008	0.205
	0.04	25.00	0.0016	214.3	1.022	0.270
	0.06	16.66	0.0036	133.6	1.035	0.290
298	0.08	12.50	0.0064	94.7	1.050	0.307
	0.1	10.00	0.01	71.8	1.066	0.326
	0.12	8.33	0.0144	59.9	1.088	0.326
	0.15	6.66	0.0225	46.2	1.105	0.341
	0.02	50.00	0.0004	408.7	1.011	0.283
	0.04	25.00	0.0016	186.2	1.025	0.311
	0.06	16.66	0.0036	120.2	1.039	0.322
303	0.08	12.50	0.0064	86.9	1.054	0.336
	0.1	10.00	0.01	69.9	1.068	0.335
	0.12	8.33	0.0144	57.5	1.083	0.340
	0.15	6.66	0.0225	45.5	1.106	0.345
	0.02	50.00	0.0004	320.5	1.014	0.360
	0.04	25.00	0.0016	156.1	1.030	0.371
	0.06	16.66	0.0036	105.6	1.045	0.367
308	0.08	12.50	0.0064	80.2	1.059	0.364
	0.1	10.00	0.01	64.5	1.074	0.363

	0.12	8.33	0.0144	54.3	1.088	0.360
	0.15	6.66	0.0225	43.9	1.111	0.359
	0.02	50.00	0.0004	248.2	1.019	0.466
	0.04	25.00	0.0016	133.0	1.035	0.436
	0.06	16.66	0.0036	94.3	1.050	0.412
313	0.08	12.50	0.0064	71.9	1.066	0.406
	0.1	10.00	0.01	58.9	1.081	0.398
	0.12	8.33	0.0144	50.0	1.096	0.392
	0.15	6.66	0.0225	40.7	1.120	0.387

Table 4.8

VISCOSITY DATA FOR CALCIUM NITRATE IN 10% METHANOL-WATER SOLUTIONS 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	389.4	1.012	0.296
	0.04	25.00	0.0016	195.9	1.024	0.295
	0.06	16.66	0.0036	133.6	1.035	0.289
298	0.08	12.50	0.0064	99.3	1.047	0.293
	0.1	10.00	0.01	80.3	1.059	0.290
	0.12	8.33	0.0144	66.9	1.071	0.291
	0.15	6.66	0.0225	52.9	1.091	0.296
	0.02	50.00	0.0004	314.4	1.015	0.367
	0.04	25.00	0.0016	169.9	1.027	0.341
	0.06	16.66	0.0036	117.2	1.040	0.330
303	0.08	12.50	0.0064	90.6	1.052	0.321
	0.1	10.00	0.01	73.9	1.064	0.316
	0.12	8.33	0.0144	62.1	1.077	0.314
	0.15	6.66	0.0225	51.1	1.094	0.307
	0.02	50.00	0.0004	268.3	1.017	0.431
	0.04	25.00	0.0016	152.2	1.031	0.381
	0.06	16.66	0.0036	109.2	1.043	0.355
308	0.08	12.50	0.0064	85.1	1.056	0.342

	0.1	10.00	0.01	70.5	1.068	0.332
	0.12	8.33	0.0144	59.5	1.081	0.329
	0.15	6.66	0.0225	49.1	1.098	0.320
	0.02	50.00	0.0004	237.3	1.020	0.487
	0.04	25.00	0.0016	139.2	1.034	0.417
	0.06	16.66	0.0036	101.2	1.046	0.383
313	0.08	12.50	0.0064	80.2	1.059	0.364
	0.1	10.00	0.01	66.7	1.071	0.351
	0.12	8.33	0.0144	57.4	1.083	0.340
	0.15	6.66	0.0225	47.5	1.102	0.330

Table 4.9

VISCOSITY DATA FOR CALCIUM NITRATE IN 20% METHANOL-WATER SOLUTIONS 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	287.2	1.016	0.402
	0.04	25.00	0.0016	158.5	1.029	0.370
	0.06	16.66	0.0036	111.8	1.042	0.346
298	0.08	12.50	0.0064	86.9	1.054	0.335
	0.1	10.00	0.01	71.8	1.066	0.325
	0.12	8.33	0.0144	61.0	1.078	0.320
	0.15	6.66	0.0225	49.5	1.098	0.317
	0.02	50.00	0.0004	237.3	1.012	0.487
	0.04	25.00	0.0016	137.9	1.034	0.420
	0.06	16.66	0.0036	101.1	1.047	0.383
303	0.08	12.50	0.0064	78.6	1.060	0.371
	0.1	10.00	0.01	66.2	1.072	0.354
	0.12	8.33	0.0144	57.0	1.084	0.343
	0.15	6.66	0.0225	46.9	1.103	0.335
	0.02	50.00	0.0004	212.8	1.022	0.544
	0.04	25.00	0.0016	127.5	1.037	0.455
	0.06	16.66	0.0036	94.3	1.050	0.412
308	0.08	12.50	0.0064	75.2	1.063	0.388
	0.1	10.00	0.01	62.9	1.076	0.373

	0.12	8.33	0.0144	54.2	1.089	0.361
	0.15	6.66	0.0225	45.5	1.106	0.346
	0.02	50.00	0.0004	202.2	1.023	0.572
	0.04	25.00	0.0016	123.4	1.038	0.470
	0.06	16.66	0.0036	92.4	1.051	0.420
313	0.08	12.50	0.0064	74.5	1.064	0.392
	0.1	10.00	0.01	63.9	1.075	0.367
	0.12	8.33	0.0144	57.4	1.088	0.357
	0.15	6.66	0.0225	46.2	1.105	0.341

Table 4.10

VISCOSITY DATA FOR CALCIUM NITRATE IN 30% METHANOL-WATER SOLUTIONS 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	255.9	1.018	0.452
	0.04	25.00	0.0016	148.2	1.032	0.391
	0.06	16.66	0.0036	107.9	1.044	0.359
298	0.08	12.50	0.0064	85.1	1.056	0.342
	0.1	10.00	0.01	71.2	1.067	0.328
	0.12	8.33	0.0144	60.5	1.079	0.323
	0.15	6.66	0.0225	50.3	1.096	0.312
	0.02	50.00	0.0004	210.1	1.022	0.551
	0.04	25.00	0.0016	128.9	1.036	0.450
	0.06	16.66	0.0036	97.1	1.049	0.400
303	0.08	12.50	0.0064	76.5	1.062	0.381
	0.1	10.00	0.01	66.2	1.072	0.354
	0.12	8.33	0.0144	57.0	1.084	0.343
	0.15	6.66	0.0225	48.3	1.100	0.325
	0.02	50.00	0.0004	186.2	1.025	0.622
	0.04	25.00	0.0016	118.2	1.040	0.491
	0.06	16.66	0.0036	89.9	1.053	0.432
308	0.08	12.50	0.0064	72.5	1.065	0.403

	0.1	10.00	0.01	62.3	1.077	0.376
	0.12	8.33	0.0144	54.2	1.089	0.361
	0.15	6.66	0.0225	46.2	1.105	0.341
	0.02	50.00	0.0004	180.0	1.026	0.643
	0.04	25.00	0.0016	110.6	1.043	0.526
	0.06	16.66	0.0036	89.0	1.053	0.436
313	0.08	12.50	0.0064	73.2	1.065	0.399
	0.1	10.00	0.01	63.4	1.075	0.369
	0.12	8.33	0.0144	55.6	1.086	0.352
	0.15	6.66	0.0225	47.6	1.102	0.330

Table 4.11.a

Φ VALUES OF CALCIUM NITRATE IN METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURE

Mass fraction of methanol Temperature (^{o}K)	0%	10%	20%	30%
298	-62.72	8.68	66.84	81.45
303	-24.15	58.87	69.48	88.63
308	13.67	66.05	71.17	83.68
313	29.10	69.36	84.36	94.17

Table 4.11.b

$\bar{V}$ VALUES OF CALCIUM NITRATE IN METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURE

Mass fraction of methanol Temperature (^{o}K)	0%	10%	20%	30%
298	0.1116	0.1151	0.1496	0.1596
303	0.1242	0.1189	0.1727	0.1918
308	0.1463	0.1514	0.1967	0.2151
313	0.1718	0.1730	0.2015	0.2230

Table 4.12.a

M VALUES OF CALCIUM NITRATE IN METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURE

Mass fraction of methanol Temperature (°K)	0%	10%	20%	30%
298	1.035	1.034	1.041	1.045
303	1.0405	1.04	1.048	1.0505
308	1.044	1.043	1.052	1.056
313	1.049	1.047	1.052	1.053

Table 4.12.b

K' VALUES OF CALCIUM NITRATE IN METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURE

Mass fraction of methanol Temperature (°K)	0%	10%	20%	30%
298	3.12	2.58	2.5	2.5
303	2.91	2.35	2.5	2.57
308	2.93	2.5	2.38	2.29
313	3.21	2.39	2.38	2.18

Table 4.13

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

Wt. % MeOH in MeOH-H_2O		ΔE^* K cal	ΔF^* K Cal	ΔS^* e.u.
0%	Sovent (water)	3.884	2.187	5.69
	$Ca(NO_3)_2$	4.055	2.209	6.19
10%	Solvent	4.243	2.371	6.28
	$Ca(NO_3)_2$	4.405	2.392	6.76
20%	Solvent	4.691	2.520	7.29
	$Ca(NO_3)_2$	4.746	2.543	7.39
30%	Solvent	4.967	2.619	7.88
	$Ca(NO_3)_2$	5.122	2.642	8.32

Table 4.14

TRANSPORT PROPERTIES OF VISCOUS FLOW OF CALCIUM NITRATE IN 10% METHANOL-WATER SOLUTION AT 298 ^{o}K.

Concentration (M) moles/lit	ΔE^* K Cal	ΔS^* e.u.	ΔF^* K Cal
0.02	4.404	6.794	2.378
0.04	4.403	6.785	2.381
0.06	4.408	6.791	2.384
0.08	4.405	6.768	2.388
0.1	4.405	6.755	2.392
0.12	4.402	6.728	2.397
0.15	4.405	6.718	2.403

Table 4.15

IONIC PARAMETER VALUES FOR Ba^{++} AND Ca^{++} IN 0% METHANOL-WATER SOLUTION AT 298 ^{o}K.

Ion	$\overline{V}_o$	$B\pm$ in $l\ mol^{-1}$	$\overline{V}\pm$ in $cm^3\ mol^{-1}$	N_B	ΔS^* in e.u.
Ba^{++}	6.200	0.296	118.4	16.94	6.73
Ca^{++}	2.455	0.476	190.4	28.39	6.19

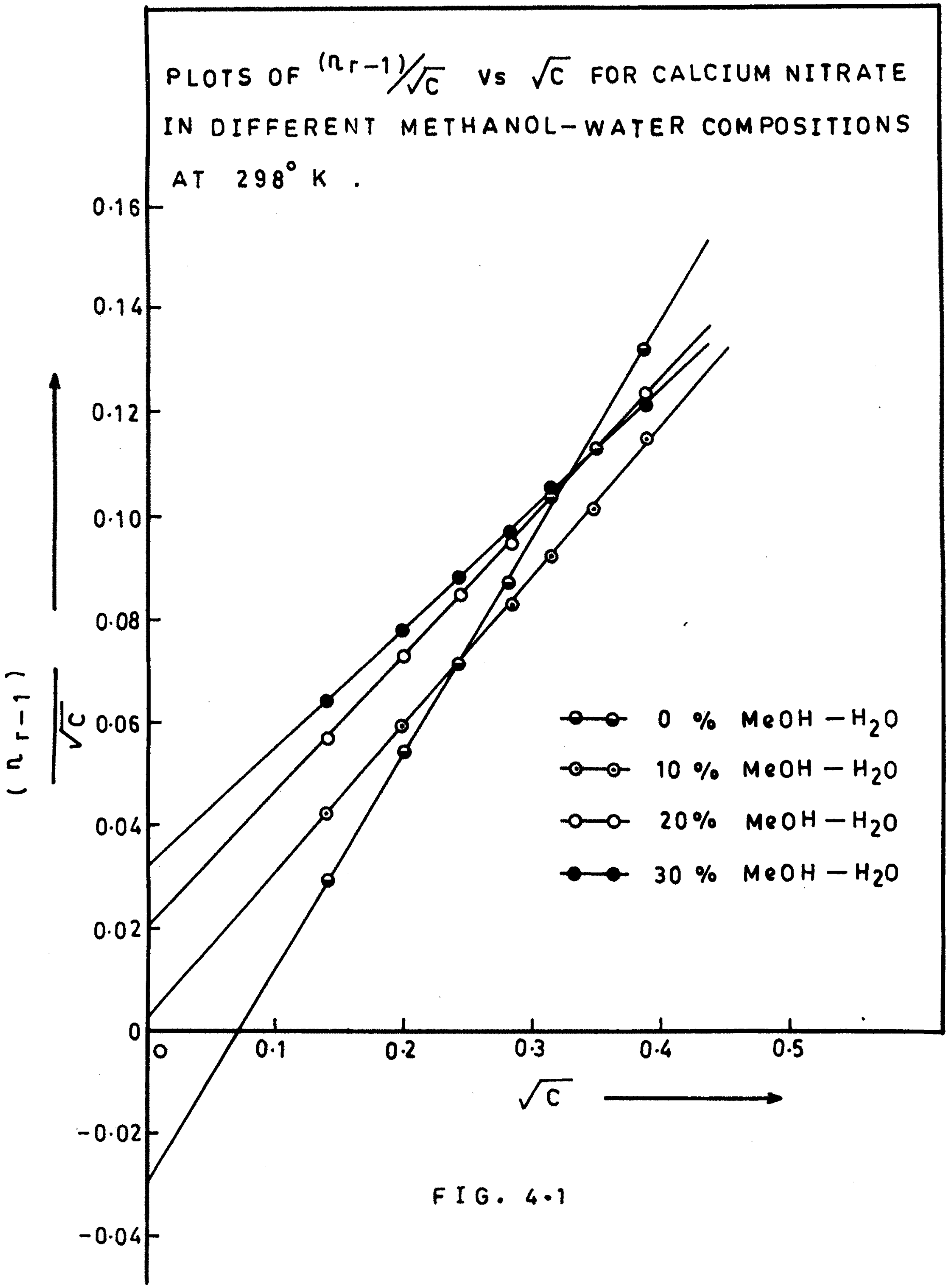
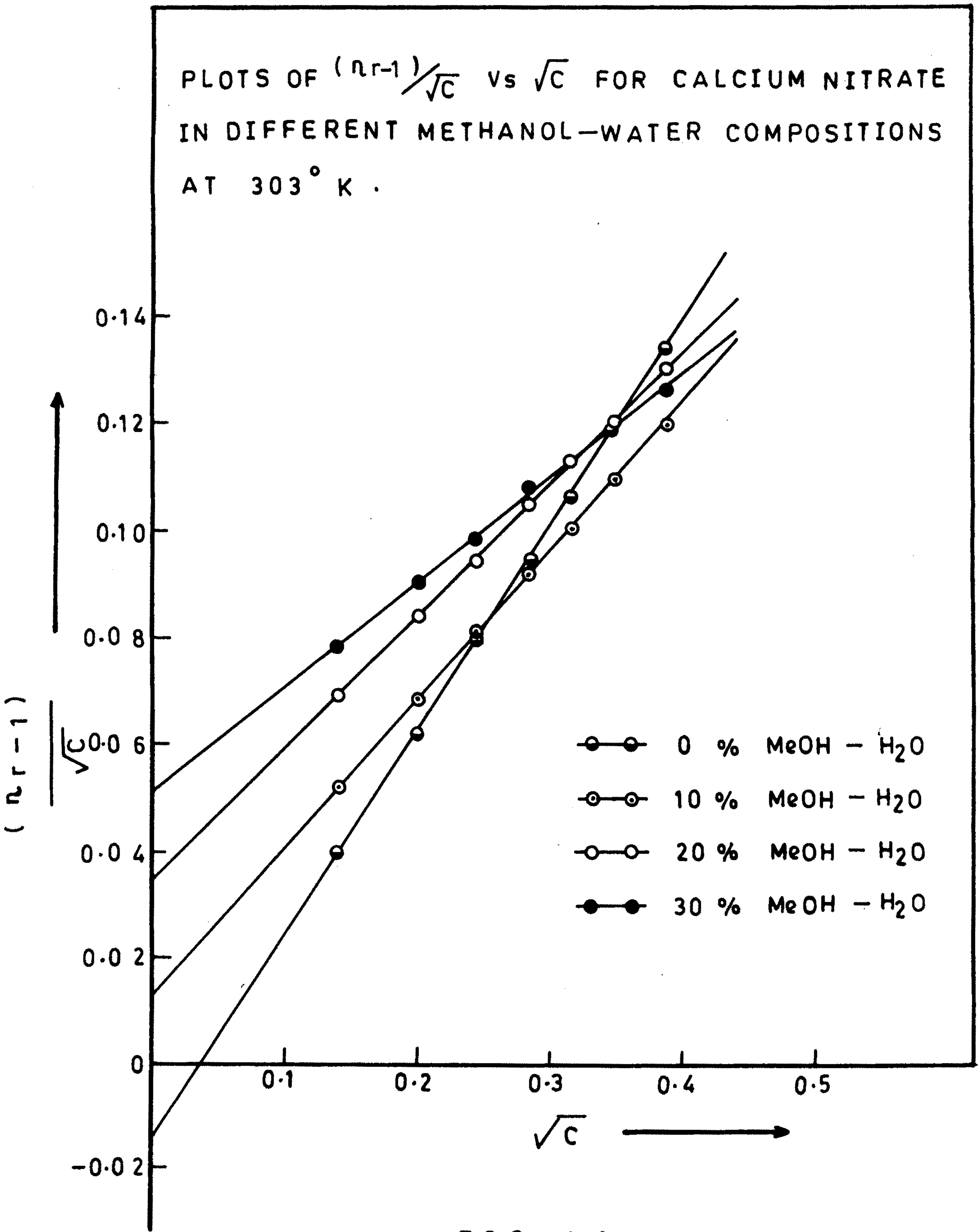

PLOTS OF $(n_r - 1)/\sqrt{C}$ Vs $\sqrt{C}$ FOR CALCIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 298° K .
0·16
0·14
0·12
0·10
0·08
0·06
0·04
0·02
0
-0·02
-0·04
$(n_r - 1)/\sqrt{C}$
O
0·1
0·2
0·3
0·4
0·5
$\sqrt{C}$
0 % MeOH — H_2O
10 % MeOH — H_2O
20 % MeOH — H_2O
30 % MeOH — H_2O

FIG. 4·1



PLOTS OF $(\eta_r - 1)/\sqrt{C}$ Vs $\sqrt{C}$ FOR CALCIUM NITRATE IN DIFFERENT METHANOL—WATER COMPOSITIONS AT 303° K.
0·14
0·12
0·10
0·0 8
0·0 6
0·0 4
0·0 2
0
−0·0 2
$(\eta_r - 1)/\sqrt{C}$
0·1
0·2
0·3
0·4
0·5
$\sqrt{C}$
0 % MeOH − H_2O
10 % MeOH − H_2O
20 % MeOH − H_2O
30 % MeOH − H_2O

FIG. 4·2

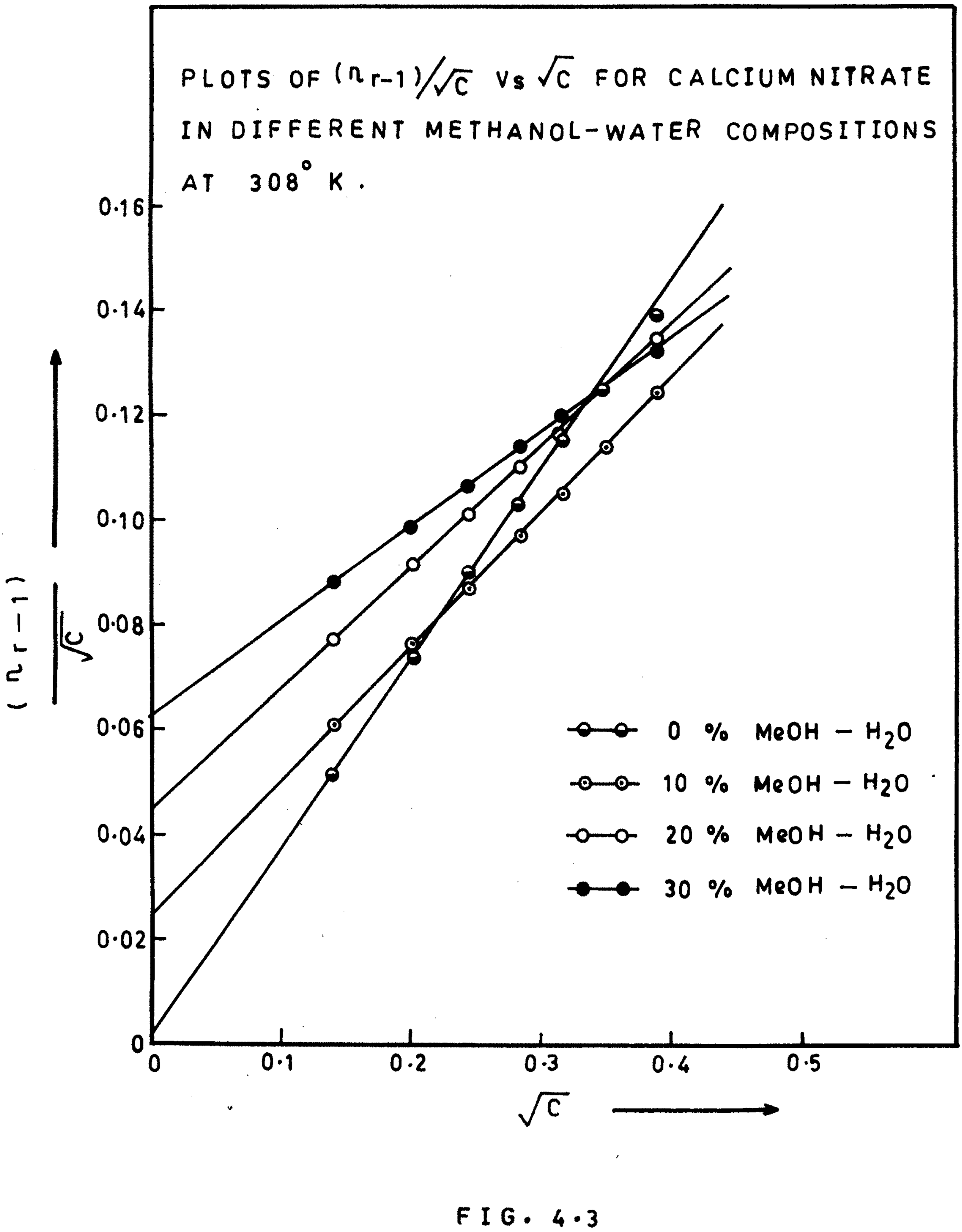
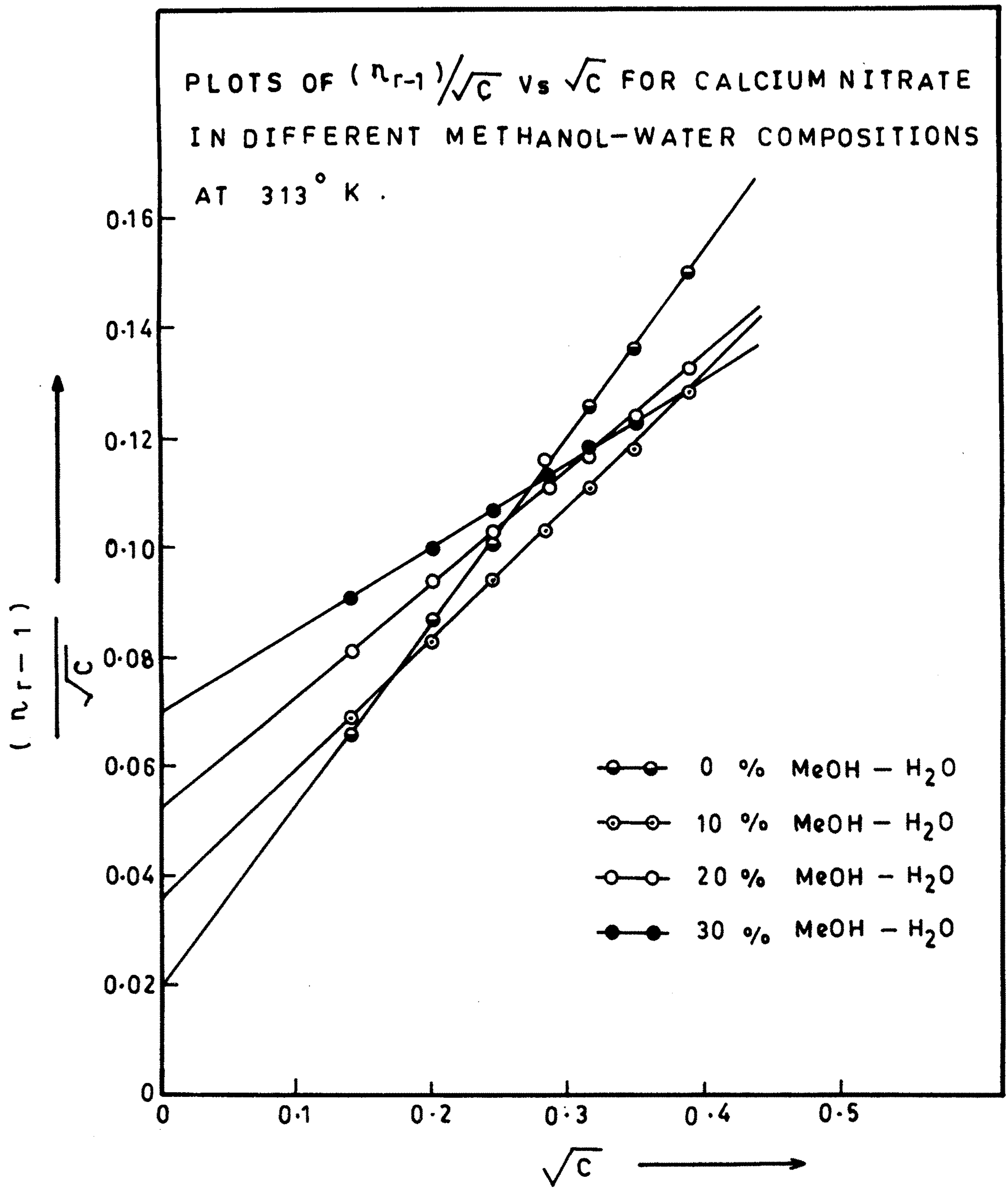
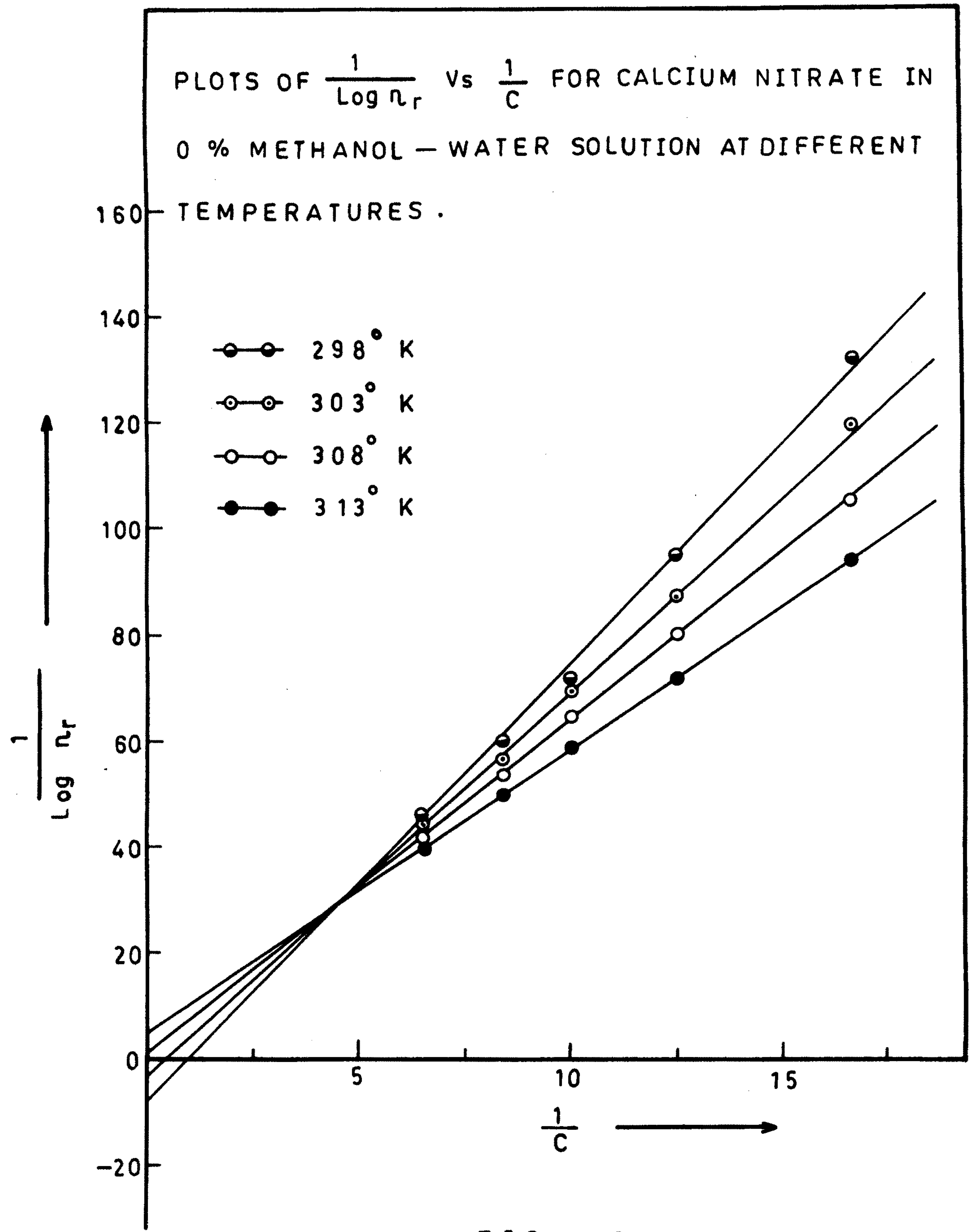

PLOTS OF $(\eta_{r}-1)/\sqrt{C}$ Vs $\sqrt{C}$ FOR CALCIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 308° K.
0·16
0·14
0·12
0·10
0·08
0·06
0·04
0·02
0
0·1
0·2
0·3
0·4
0·5
$(\eta_{r}-1)/\sqrt{C}$
$\sqrt{C}$
0 % MeOH – H_2O
10 % MeOH – H_2O
20 % MeOH – H_2O
30 % MeOH – H_2O

FIG. 4·3



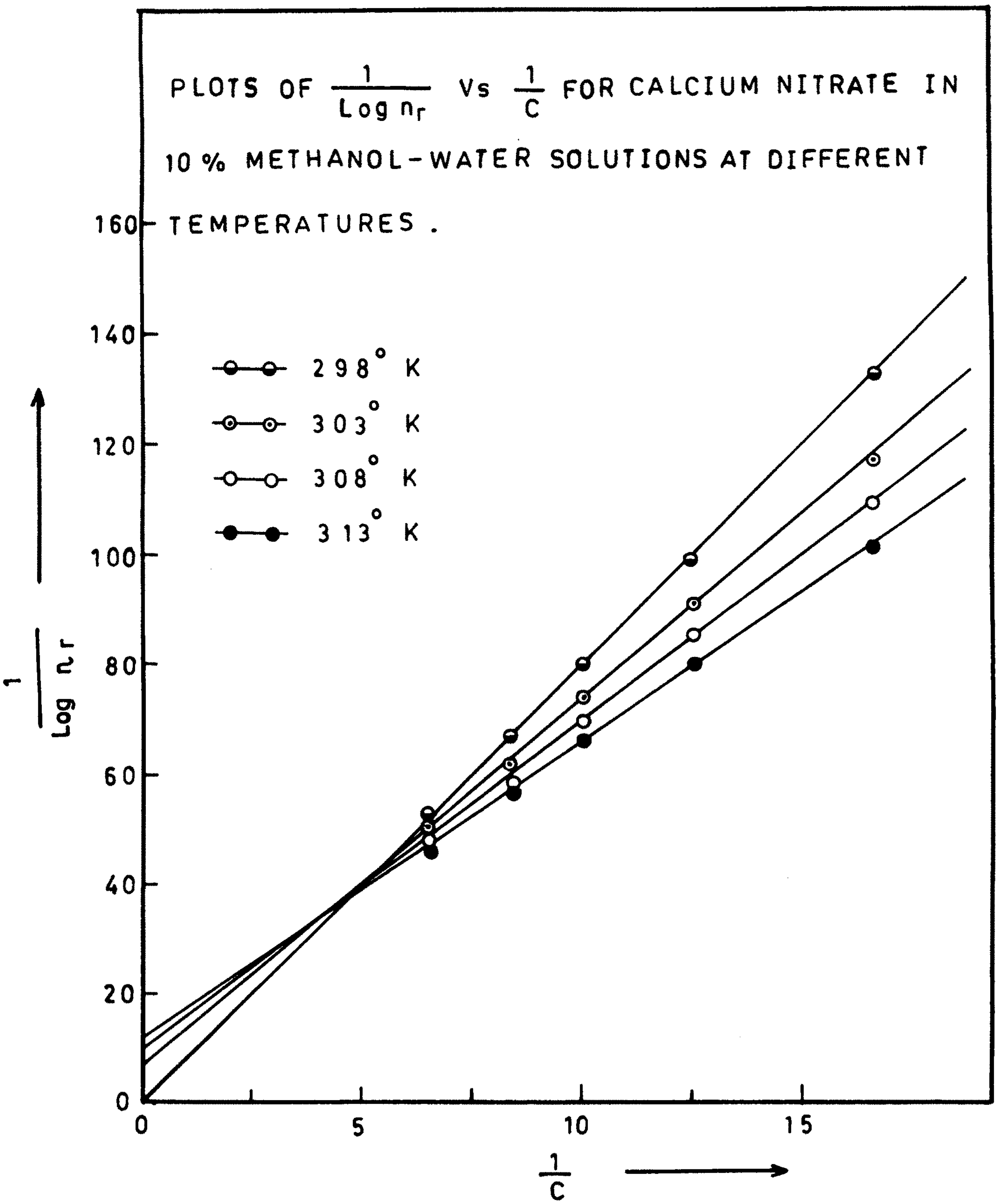
PLOTS OF $(\eta_r-1)/\sqrt{C}$ Vs $\sqrt{C}$ FOR CALCIUM NITRATE IN DIFFERENT METHANOL-WATER COMPOSITIONS AT 313° K.
0·16
0·14
0·12
0·10
0·08
0·06
0·04
0·02
0
0·1
0·2
0·3
0·4
0·5
$(\eta_r - 1)/\sqrt{C}$
$\sqrt{C}$
0 % MeOH – H_2O
10 % MeOH – H_2O
20 % MeOH – H_2O
30 % MeOH – H_2O

FIG. 4·4



PLOTS OF $\frac{1}{\text{Log } \eta_r}$ Vs $\frac{1}{C}$ FOR CALCIUM NITRATE IN
0 % METHANOL — WATER SOLUTION AT DIFFERENT
TEMPERATURES.
298° K
303° K
308° K
313° K
160
140
120
100
80
60
40
20
0
-20
5
10
15
$\frac{1}{\text{Log } \eta_r}$
$\frac{1}{C}$

FIG. 4.5


PLOTS OF $\frac{1}{\text{Log } n_r}$ Vs $\frac{1}{C}$ FOR CALCIUM NITRATE IN 10 % METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURES .
298° K
303° K
308° K
313° K
160
140
120
100
80
60
40
20
0
$\frac{1}{\text{Log } n_r}$
0
5
10
15
$\frac{1}{C}$

F I G. 4·6

PLOTS OF $\frac{1}{\text{Log } \eta_r}$ Vs $\frac{1}{C}$ FOR CALCIUM NITRATE IN 20 % METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURES .

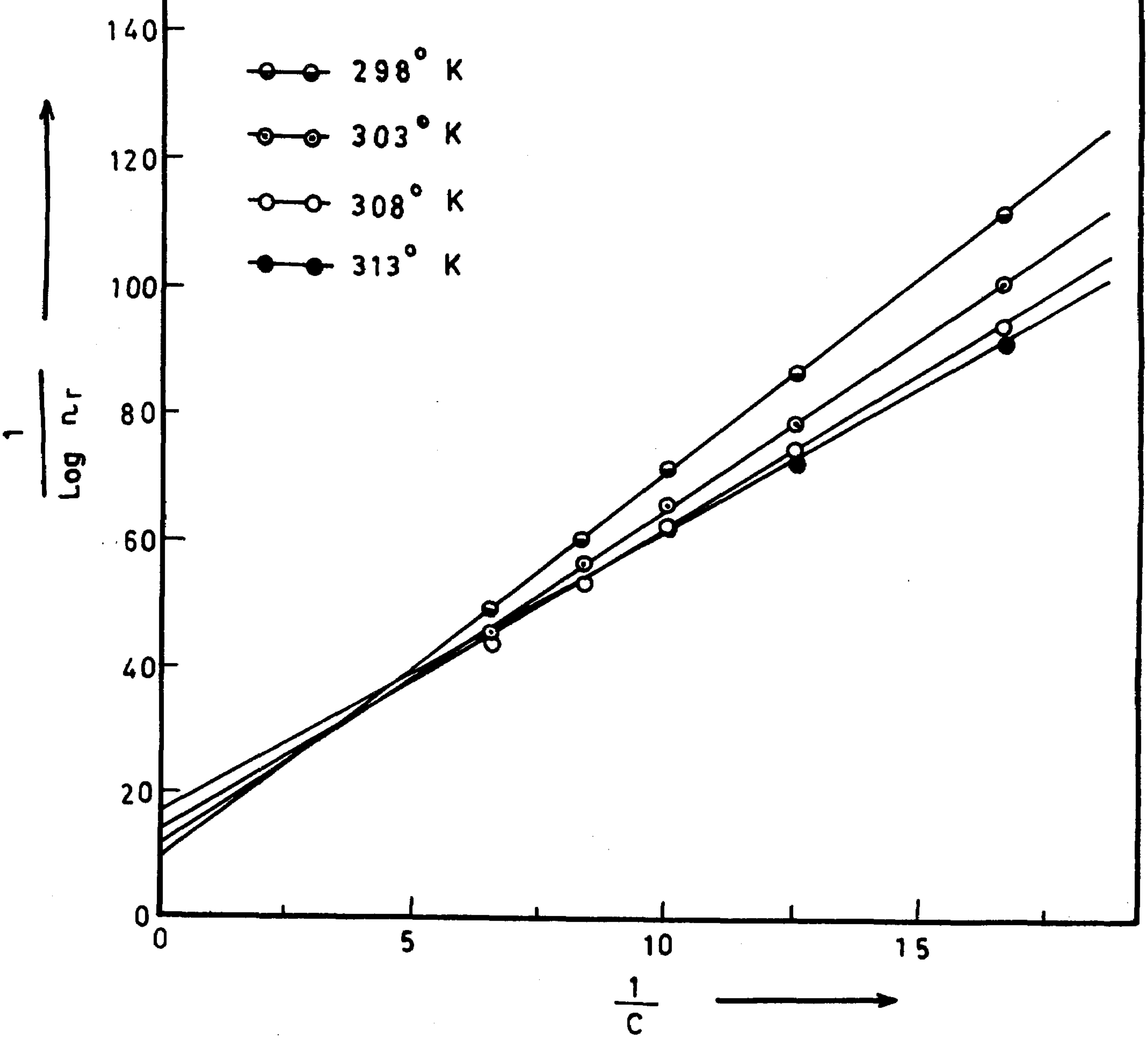


FIG. 4·7

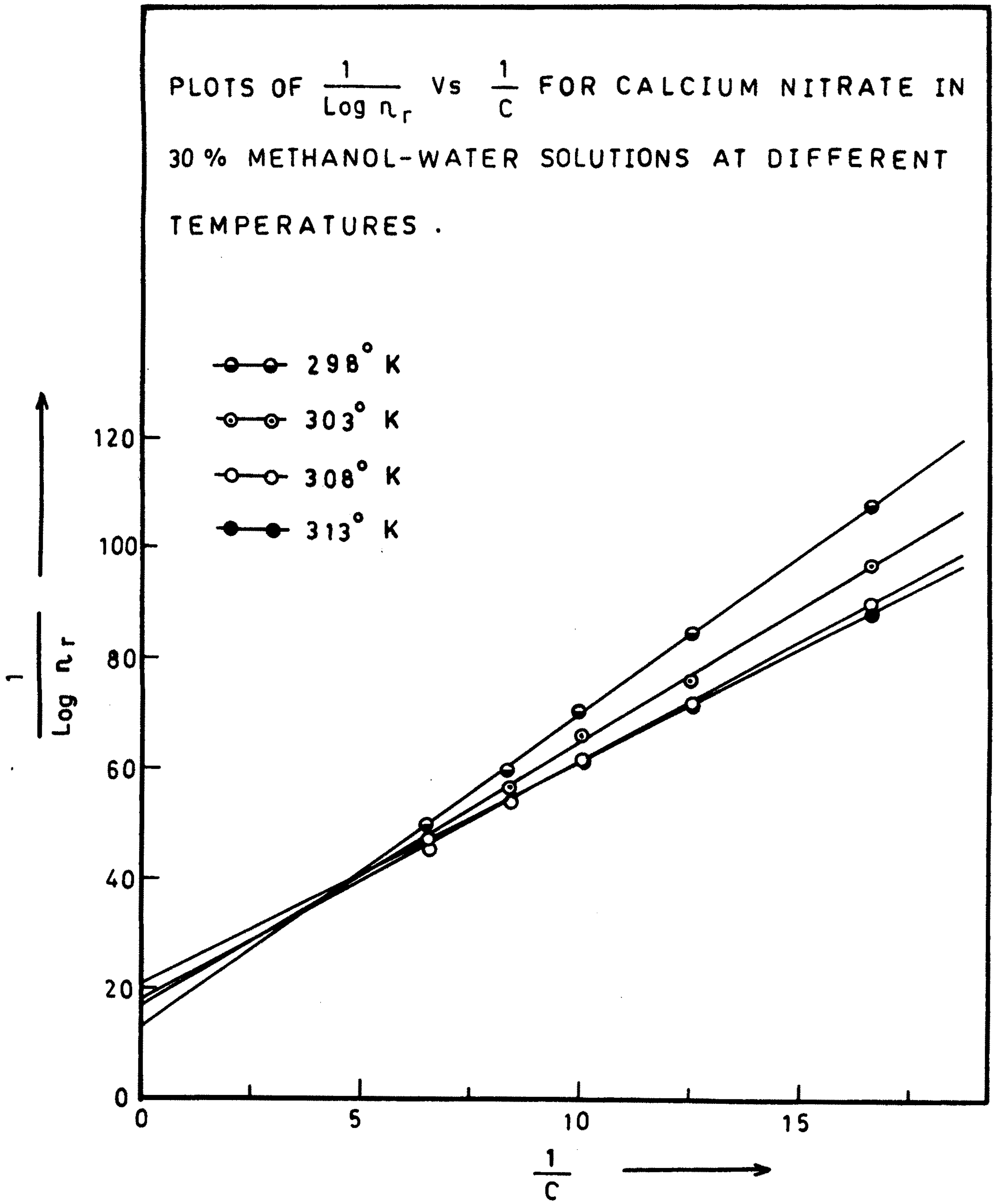

PLOTS OF $\frac{1}{\text{Log } \eta_r}$ Vs $\frac{1}{C}$ FOR CALCIUM NITRATE IN 30 % METHANOL-WATER SOLUTIONS AT DIFFERENT TEMPERATURES .
298° K
303° K
308° K
313° K
120
100
80
60
40
20
0
5
10
15
$\frac{1}{\text{Log } \eta_r}$
$\frac{1}{C}$

FIG. 4·8

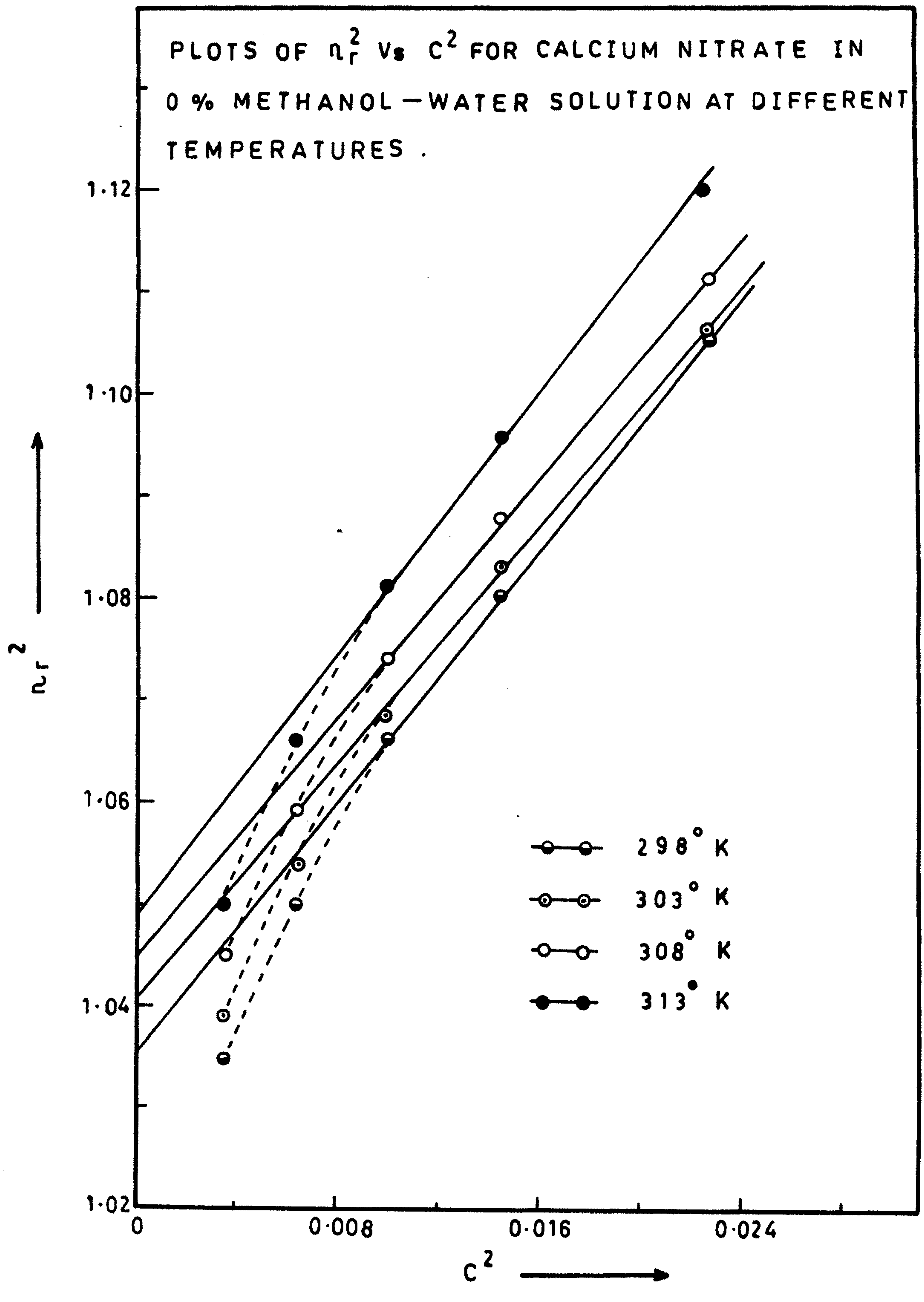
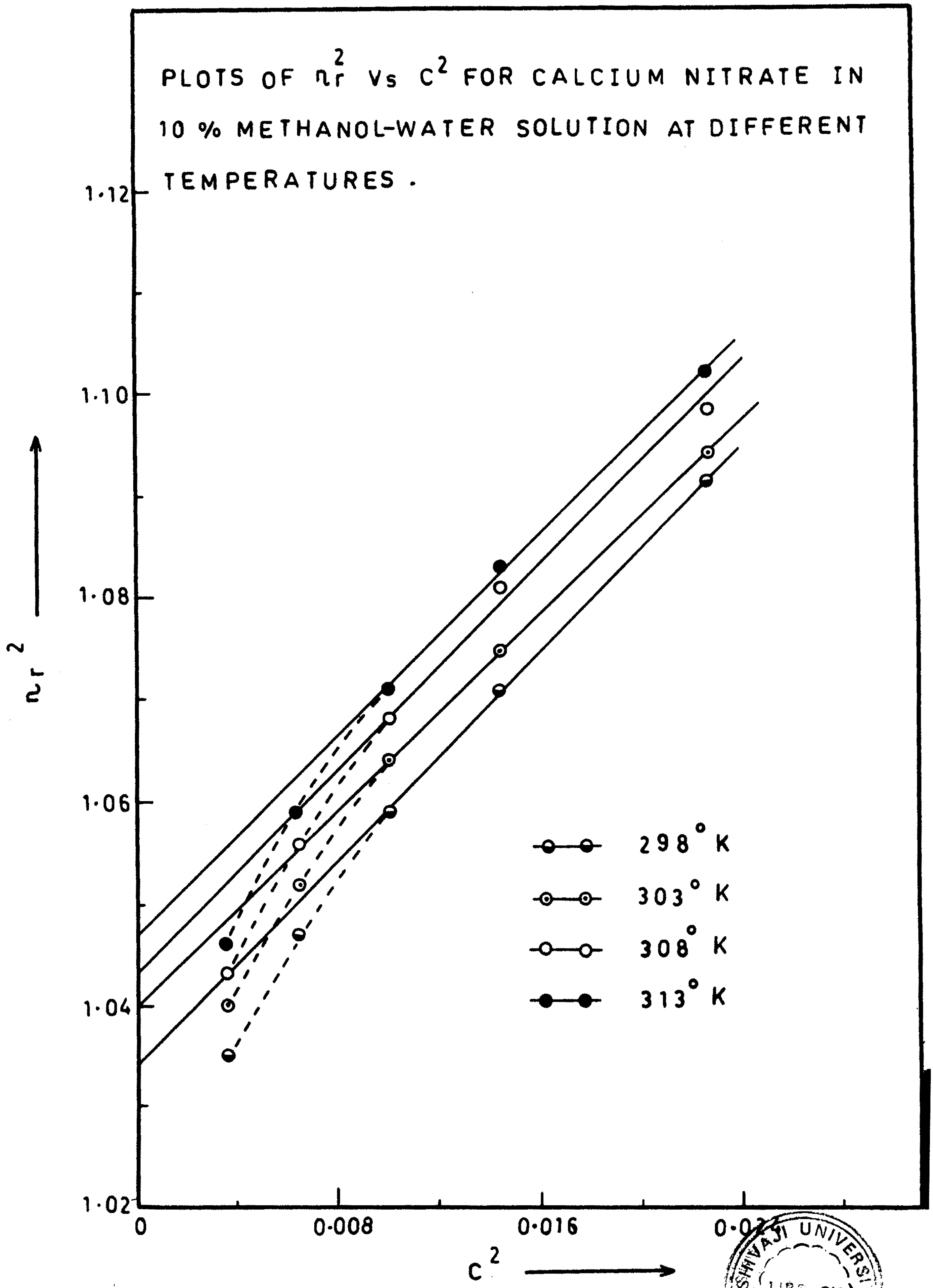

PLOTS OF η_r^2 Vs C^2 FOR CALCIUM NITRATE IN
0 % METHANOL—WATER SOLUTION AT DIFFERENT
TEMPERATURES.
1·12
1·10
1·08
1·06
1·04
1·02
0
0·008
0·016
0·024
η_r^2
C^2
298° K
303° K
308° K
313° K

FIG. 4·9



PLOTS OF ηr² Vs C² FOR CALCIUM NITRATE IN 10 % METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES .
1·12
1·10
1·08
1·06
1·04
1·02
ηr²
0
0·008
0·016
0·02
C²
298° K
303° K
308° K
313° K

FIG. 4·10

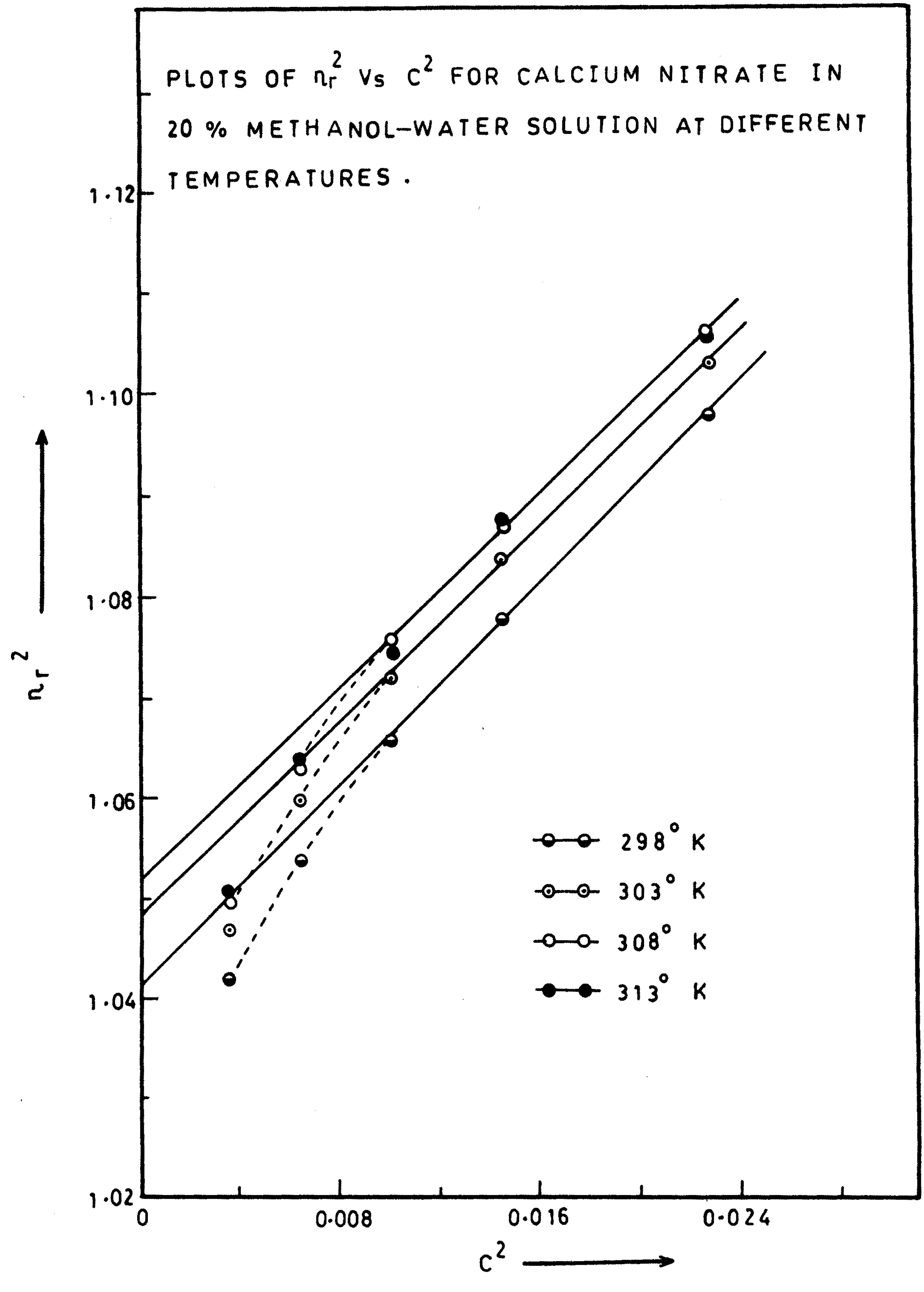

PLOTS OF η_r^2 Vs C^2 FOR CALCIUM NITRATE IN 20 % METHANOL–WATER SOLUTION AT DIFFERENT TEMPERATURES.
1·12
1·10
1·08
1·06
1·04
1·02
η_r^2
0
0·008
0·016
0·024
C^2
298° K
303° K
308° K
313° K

FIG. 4·11

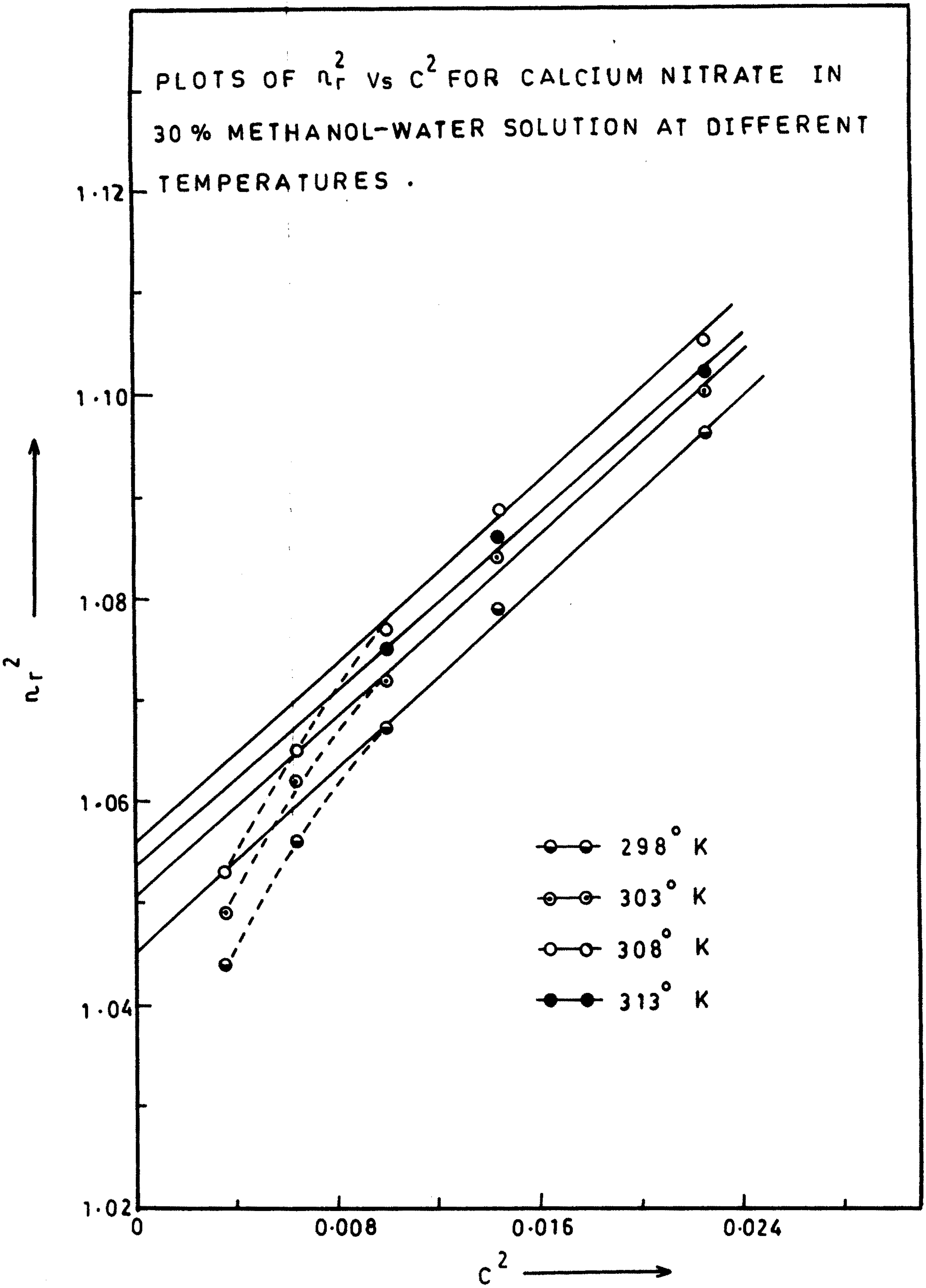

PLOTS OF η_r^2 Vs C^2 FOR CALCIUM NITRATE IN 30% METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.
1·12
1·10
1·08
1·06
1·04
1·02
η_r^2
0
0·008
0·016
0·024
C^2
298° K
303° K
308° K
313° K

FIG. 4·12

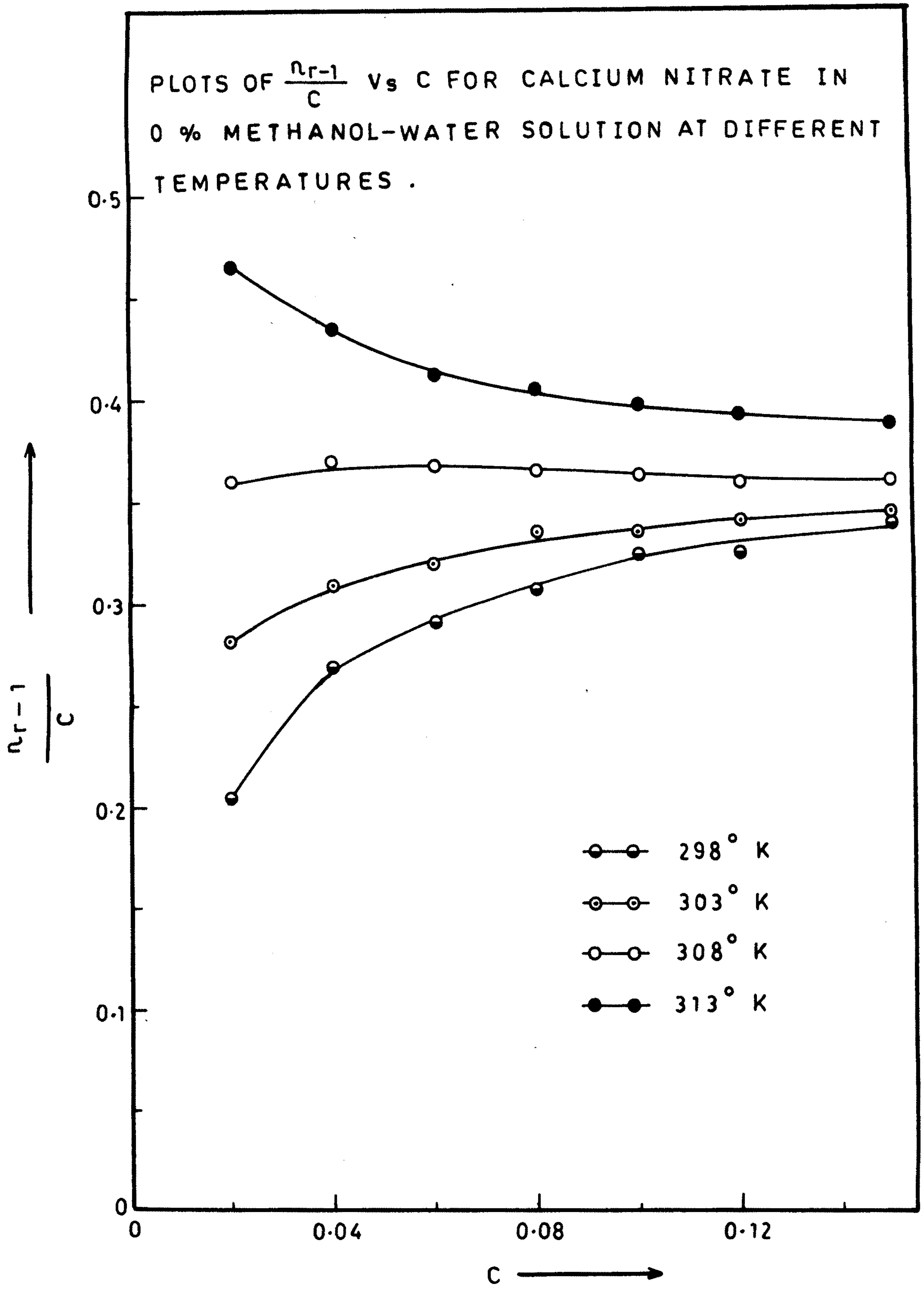

PLOTS OF $\frac{\eta_{r-1}}{C}$ Vs C FOR CALCIUM NITRATE IN 0 % METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.
0·5
0·4
0·3
0·2
0·1
0
$\frac{\eta_{r-1}}{C}$
0
0·04
0·08
0·12
C
298° K
303° K
308° K
313° K

FIG. 4·13

PLOTS OF $\frac{\eta_{r}-1}{C}$ Vs C FOR CALCIUM NITRATE IN 10 % METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.

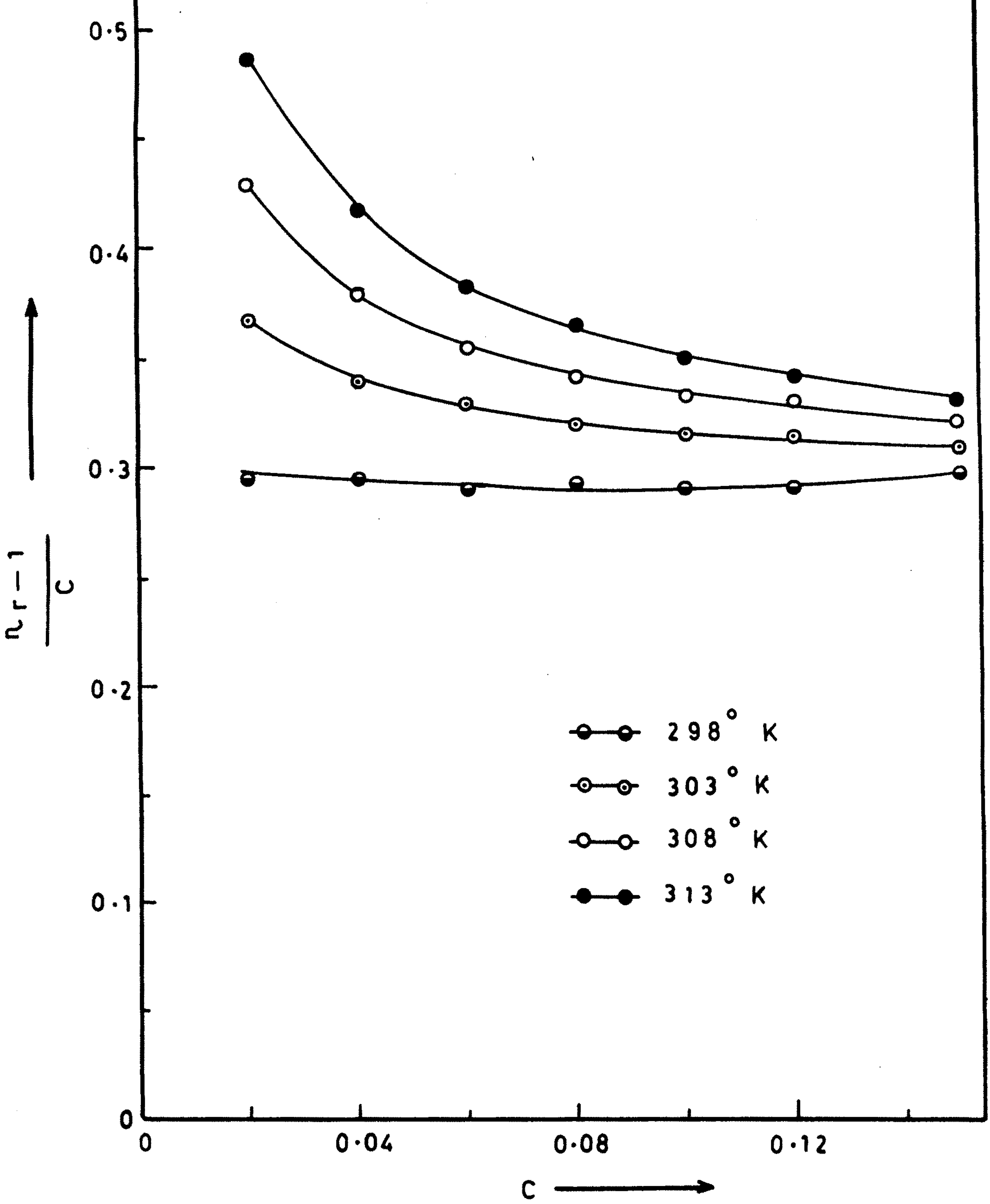
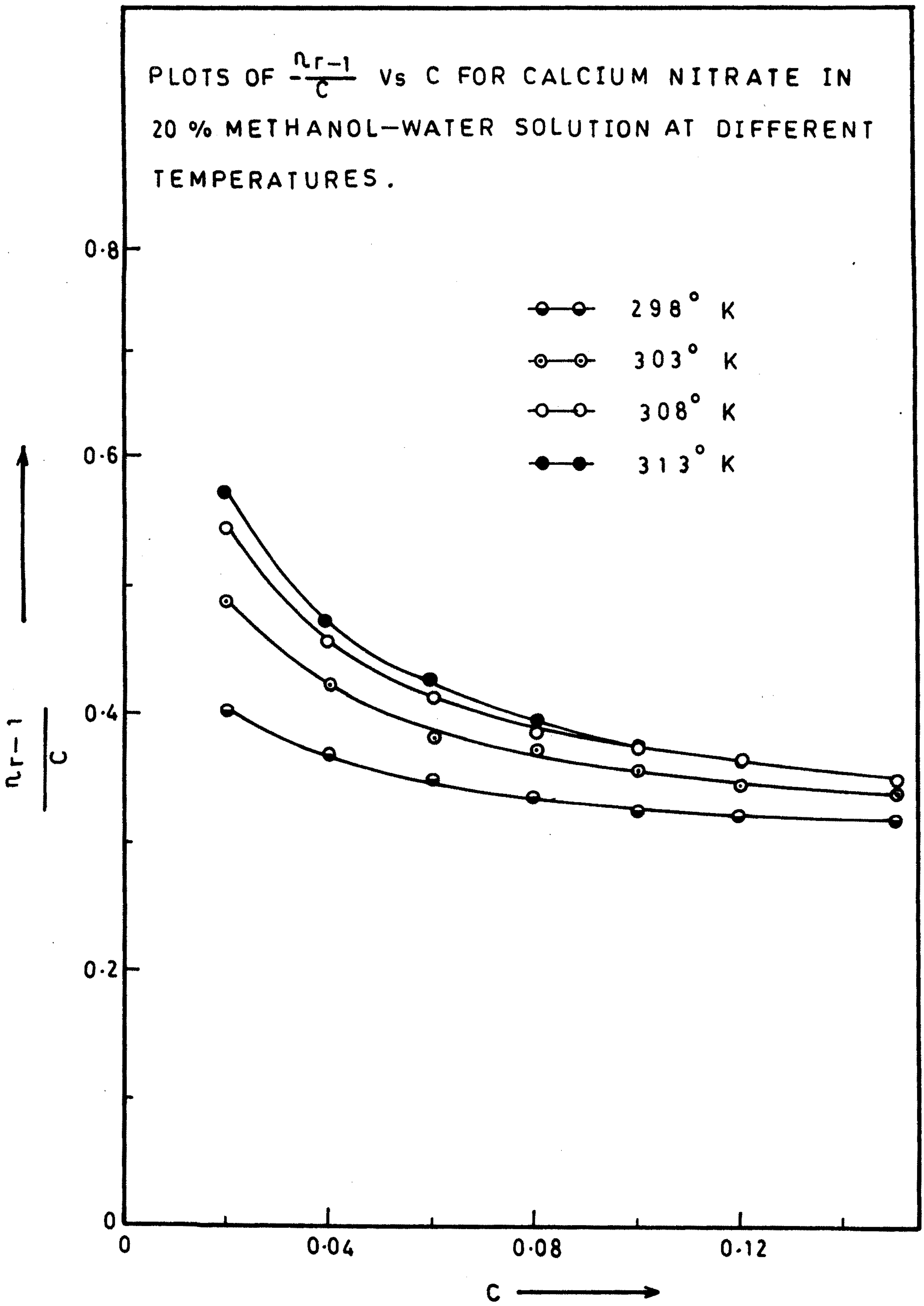


FIG. 4·14



PLOTS OF $\frac{\eta_{r}-1}{C}$ Vs C FOR CALCIUM NITRATE IN 20 % METHANOL—WATER SOLUTION AT DIFFERENT TEMPERATURES.
298° K
303° K
308° K
313° K
0·8
0·6
0·4
0·2
0
0·04
0·08
0·12
$\frac{\eta_{r}-1}{C}$
C

FIG. 4·15

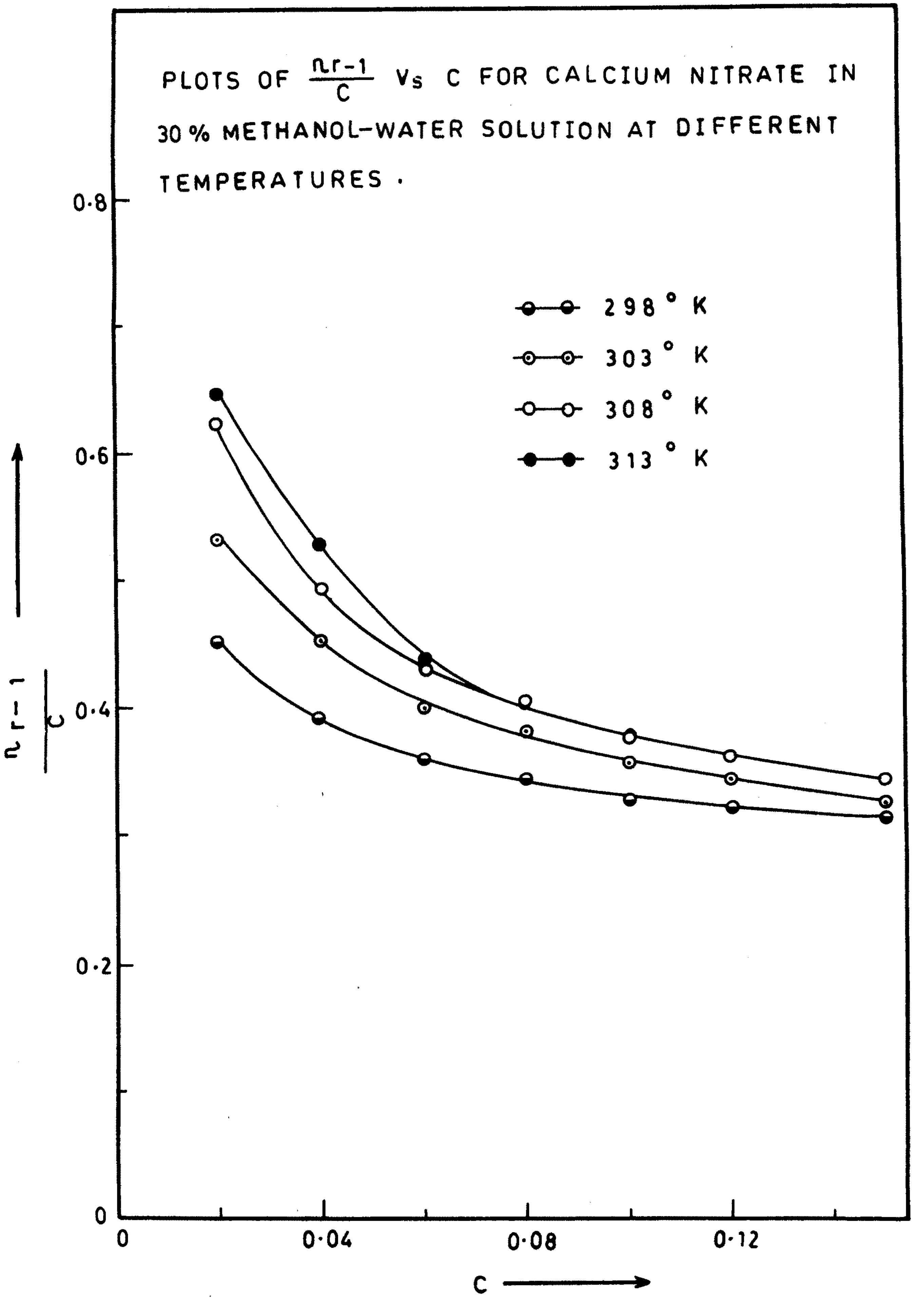

PLOTS OF $\frac{\eta r-1}{C}$ Vs C FOR CALCIUM NITRATE IN 30 % METHANOL-WATER SOLUTION AT DIFFERENT TEMPERATURES.
298 ° K
303 ° K
308 ° K
313 ° K
0·8
0·6
0·4
0·2
0
$\frac{\eta r-1}{C}$
0
0·04
0·08
0·12
C

FIG. 4·16