CHAPTER 6

GENERAL DISCUSSION

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Conductivity measurements have been carried out for the electrolytes lithium sulphate, sodium sulphate and potassium sulphate in ethanol-water, methanol-water and acetone-water mixed solvents at six different temperatures viz. 5, 10, 15, 20, 25 and 30°c. The composition of non-aqueous solvents used were 0, 10, 20, 30, 40, 50, 60, 70, 80 and 90%. The concentrations of electrolytes used in ethanol-water were $1x10^{-2}$M, $5x10^{-3}$M, $1x10^{-3}$M, $1x10^{-4}$M,$5x10^{-5}$M,$1x10^{-5}$M. For methanol-water, the concentrations were $1x10^{-2}$M, $5x10^{-3}$M, $1x10^{-3}$M, $5x10^{-4}$M, $1x10^{-4}$M, while for acetone-water, the concentrations were $1x10^{-3}$M, $5x10^{-4}$M, $1x10^{-4}$, $5x10^{-5}$M and $1x10^{-5}$M.

In case of ethanol-water system a minimum in molar conductivity has been observed at temperature 5 and 10°c for the concentrations $1x10^{-4}$M, $5x10^{-5}$M and $1x10^{-5}$M. There is regular decrease in conductivity at temperatures 15, 20, 25 and 30°c. Similarly, for the higher concentrations ($1x10^{-2}$M, $5x10^{-3}$M, $1x10^{-3}$M) for lithium sulphate and $1x10^{-3}$M and $1x10^{-4}$M for sodium-sulphate and potassium sulphate the conductivity minima have not been observed at all the temperatures studied. A regular decrease in molar conductivity values has been observed for all the temperatures studied.

In case of methanol-water systems the minimum in conductivity has been observed, not only at 5 and 10°c but also at higher temperatures 15, 20, 25 and 30°c, and for the concentrations studied, namely $1x10^{-2}$M, $5x10^{-3}$M and $1x10^{-3}$M for lithium sulphate, $1x10^{-3}$M, $5x10^{-4}$M for sodium sulphate and $5x10^{-4}$M, $1x10^{-4}$M for potassium sulphate. While there is decrease in conductivity continusously for the concentrations of $5x10^{-3}$M for sodium sulphate and $1x10^{-3}$M for potassium sulphate at all the temperatures studied.

In acetone-water binary solvents the conductivity does not pass through minimum for the concentration 1x10^{-3}M, 5x10^{-4}M for lithium sulphate, 1x10^{-3}M, 1x10^{-4}M for sodium sulphate. 1x10^{-4}M for potassium sulphate. It has been observed that molar conductivity values decreases sharply beyond 80% of acetone. The molar conductivity values pass through minimum at low temperature i.e. at 5 and 10^{o}c in case of lithium sulphate (1x10^{-4}M, 5x10^{-5}M) for sodium sulphate (5x10^{-5}M, 1x10^{-5}M). But for potassium sulphate (5x10^{-5}M, 1x10^{-5}M) the minimum is obtained for all the six temperatures studied.

It seems that the minimum is conductivity at all temperatures in methanol-water system is due to structure breaking of water and establishmnet of new hydrogen bonds to form methanol-water clusters. The clustering is favoured only at 5 and 10^{o}c in the case of ethanol-water system and for the concentrations 1x10^{-4}M, 5x10^{-5}M at lithium sulphate, 5x10^{-5}M and 1x10^{-5}M of sodium sulphate and potassium sulphate. The clustering of acetone-water is favoured at all the temperatures from 5 to 30^{o}c in case of potassium sulphate for concentration 5x10^{-5}M. The clustering is favoured at 5 and 10^{o}c for the concentration 1x10^{-4}M, 5x10^{-5}M of lithium sulphate 5x10^{-5}M, 1x10^{-5}M, 1x10^{-5}M of sodium sulphate.

When an electrolyte like lithium sulphate is dissolved in mixed solvents such as ethanol-water, lithium sulphate dissociates less, lithium and sulphate ions and get attached themselves to water molecules and ethanol molecules. This results to the division of lithium sulphate in water and ethanol. The ions attached to water molecules show very high conductance as compared to the ions attached to ethanol molecules and therefore lithium sulphate in water mainly contributing towards conductance. The number of solvents molecules in association with ions should depend upon the composition of solvent mixtures. Hence as the percentage of non-aqueous solvent increases, the conductivity decreases.

Conductivity is dependent on the nature and velocity of ions. Hence dimintion in fluidity of solvent, which would bring about a corresponding decrease in ionic mobility is an important factor resulting the minimum in conductivity. The change in ionic atmosphere which surrounds the ion is also an important factor in causing the minimum in conductivity.

An explanation that can be offered to account for the minimum in conductivity is that in these associated solvents, each solvent diminishes the association of the other, since the dissociating power is a function of the association in the solvent any thing that will diminish the association will diminish the dissociating power. The effect of mixing two associating solvents would then dissociates less than either alone and the conductivity of an electrolyte in such a mixture would be less than that in pure solvent and the molar conductivity curve if plotted against the percentage of non-aqueous solvent would pass through a minimum.

When an electrolyte is added in a concentrated form the dielectric constant of medium decreases rapidly with the result that dissociating power of electrolyte in mixed solvent becomes less and conductivity decrease is observed throughout the entire composition range and therefore no minimum in molar conductivity is observed. Martin (1929-34-37), Kirkwood (1934) and Bell (1935).

after studying static dielectric constant of alcohol-water mixtures have shown that lowering of static dielectric constant values takes place than the additive values but this can not be related directly to the structural complexities. Hence, characteristic of lowering molar conductivity in alcohol-water mixtures may not be attributed entirely to the changes in the dielectric constant though dielectric constant is one of the important factors that can effect the electrical conductivity.

As temperature is increased the association of mixed solvents decreases because hydrogen bond which exists in between two molecules is broken, this results in decrease in conductivity continously throughout composition range.

Various workers have observed that there is a close relation between conductivity minimum and viscosity maximum. The minima and maxima are more pronounced at lower temperatures and lower concentrations. The static dielectric constant of medium decrease with increase in concentration of non aqueous solvent. The recent work of viscosity in entire range of acetone-water, ethanol-water and methanol-water mixed solvent shows that viscosity is maximum in the range of 40 to 60 percent non-aqueous solvent. Leu (1979) has shown thet viscosity for ethanol-water system is 2.5 times of ethanol or water at 70% ethanol dilution. Therefore, qualitively it can be interpreted that the decrease in conductivity of an electrolyte when dissolved in mixed solvent is partly due to less dissociation. (due to decrease in dielectric constant of the solvent) of electrolyte in binary mixed solvent and partly due to increase in the viscosity. However all these effects need to be explained in terms of structure of mixed solvents. When an alcohol is added to water, the water structure is broken but new hydrogen bonds are establishe in order to form alcohol-water clusters. These clusters help to decrease the ionic mobility, resulting into, increase in viscosity and decrease in conductivity of solution. The number of such clusters increases with increasing concentration of ethanol or non-aqueous solvent and if number of clusters is maximum at 70% ethanol water then minimum can be explained.

The systems studied at six different temperatures indicate that molar conductivity values increase linearly with temperature. This can be seen from the number of temperature - molar conductivity graphs at the end of each system. The volume contration of each mixture has been determined while preparing the solutions at 30°c. The volume contration is maximum in the composition range 50 to 70% at non-aqueous solvents and it has nearly the same values in this range. This may be the proof of association factor which causes minimum in conductivity. The volume contration is found to be same for ethanol-water and methanol-water. The volume contration in the case of acetone-water systems is higher than alcohol -water systems. This may be due to more association of acetone and water. The volume contration is found to be independent of concentration ~~of~~ and nature of salt. This can be seen from the following table.

Volume contration of water-ethanol, water-methanol, and water-acetone with sodium sulphate as a salt at 30°c.

Non aq-solvent	Volume decreases on mixing in ml/250 ml		
	ETHANOL	METHANOL	ACETONE
10	2.4	2.5	3.3
20	4.7	4.7	5.7
30	6.8	7.0	7.6
40	7.4	7.5	9.6
50	8.8	9.0	10.1
60	8.9	9.0	10.2
70	8.9	8.8	9.8
80	7.5	7.5	9.0
90	5.2	5.3	7.0

The study of conductivity of all the three electrolytes namely lithium sulphate, sodium sulphate, and potassium sulphate in ethanol-water, methanol-water and acetone-water mixed solvents reveals that molar conductivity values obey the order -

acetone-water > methanol-water > ethanol-water

upto 70% of non-aqueous solvents. Above this percentage the order changes as -

methanol-water > acetone-water > ethanol-water

The reason for the change in order can be attributed to the following factors

a) The association of acetone-water is higher than alcohol water.

b) The viscosity of acetone-water medium is lower than methanol-water medium.

c) The static dielectric constant of methanol-water medium is higher than acetone-water.

The molar conductivity of the alkali metal sulphates in general obey the order : $Li_2SO_4 < Na_2SO_4 < K_2SO_4$

It has been found that the specific conductance increases from Li to K as the atomic size increases. The result obtained also showed that the plots of ionic raddii of lithium, sodium, potassium ions against specific conductance are straight lines, as can be seen by the suumary graphs, (6.1 to 6.18).

The values of ionic radii ($Li^+ = 6.8$ A°, $Na^+ = 9.8$ A°, $K^+ = 13.3$ A°) are taken from Lange's Hand book of Chemistry (twelth edition).

The results obtained can also be confirmed by other physio-chemical properties such as viscosity, surface-tension, spectrophotometry etc. The author intends to continue this line of research.

SYSTEM : ALKALI METAL SULPHATES [1×10^{-3}M]

SOLVENT : METHANOL-WATER , TEMP : 5°C

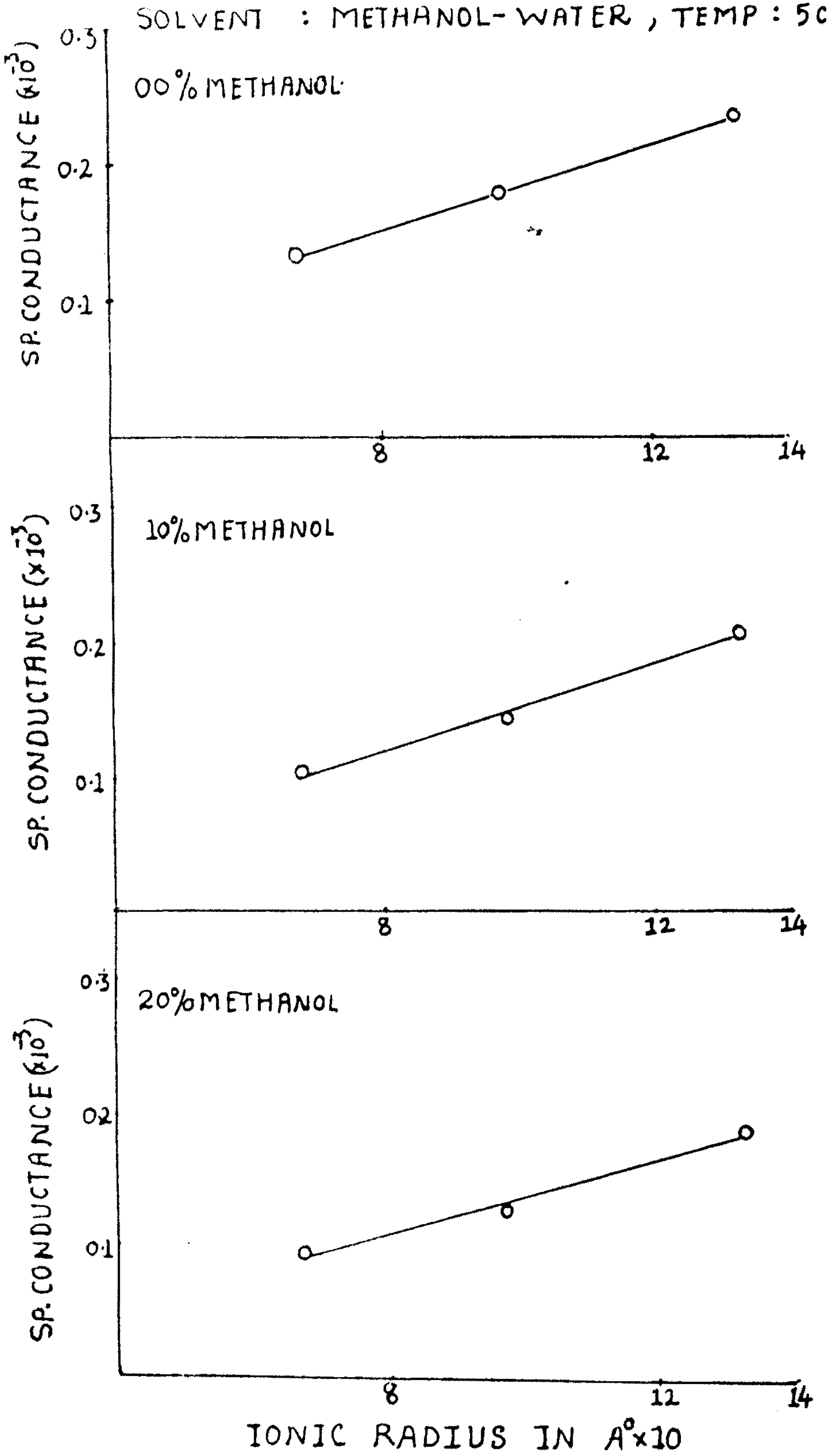


FIG- 6-1

SYSTEM : ALKALI METAL SULPHATES [1×10^{-3}M]

SOLVENT: METHANOL-WATER, TEMP: 5°C

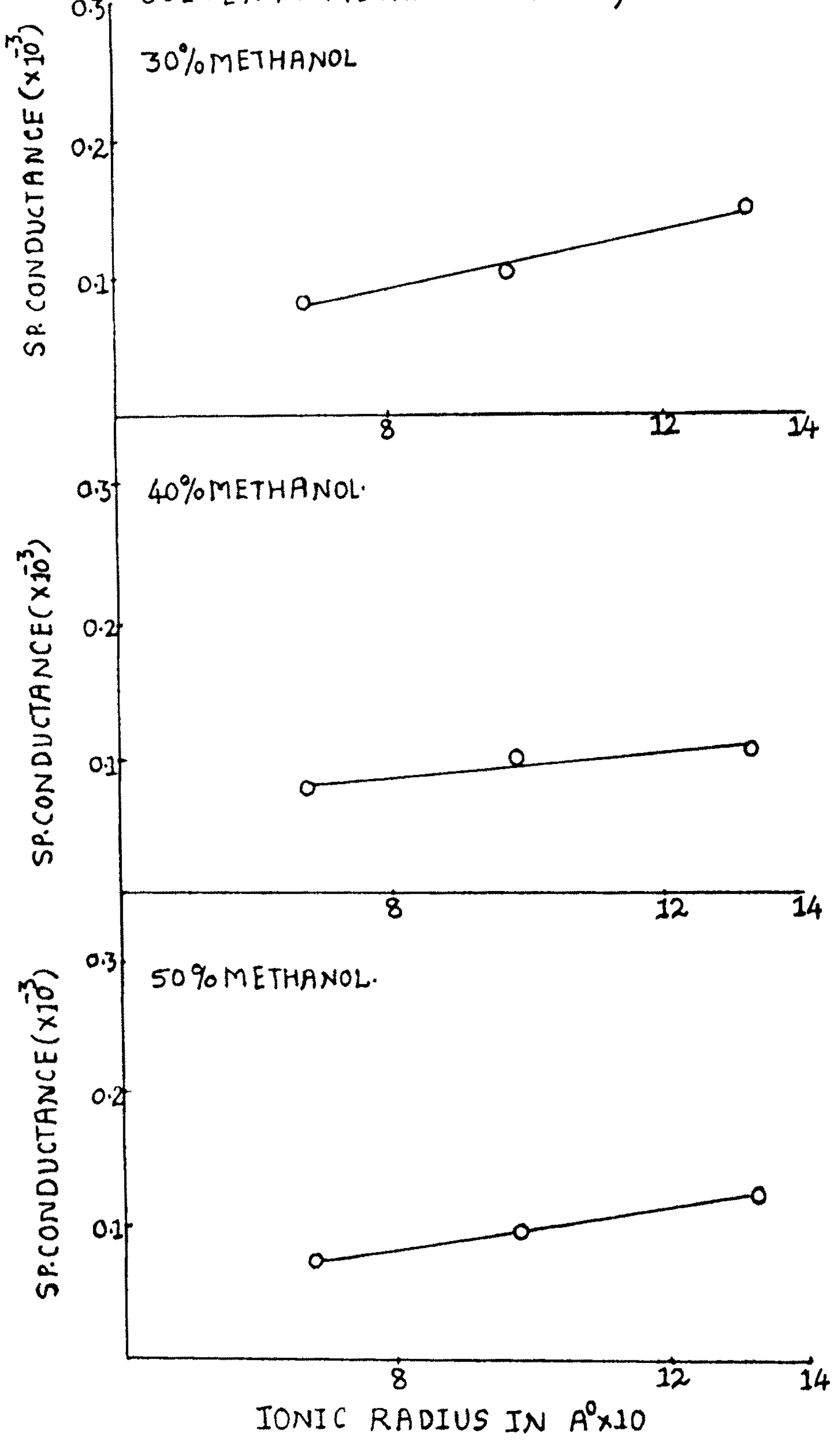


FIG-6.2

SYSTEM : ALKALI METAL SULPHATES [1×10^{-3} M]

SOLVENT : METHANOL-WATER , TEMP: 5°C.

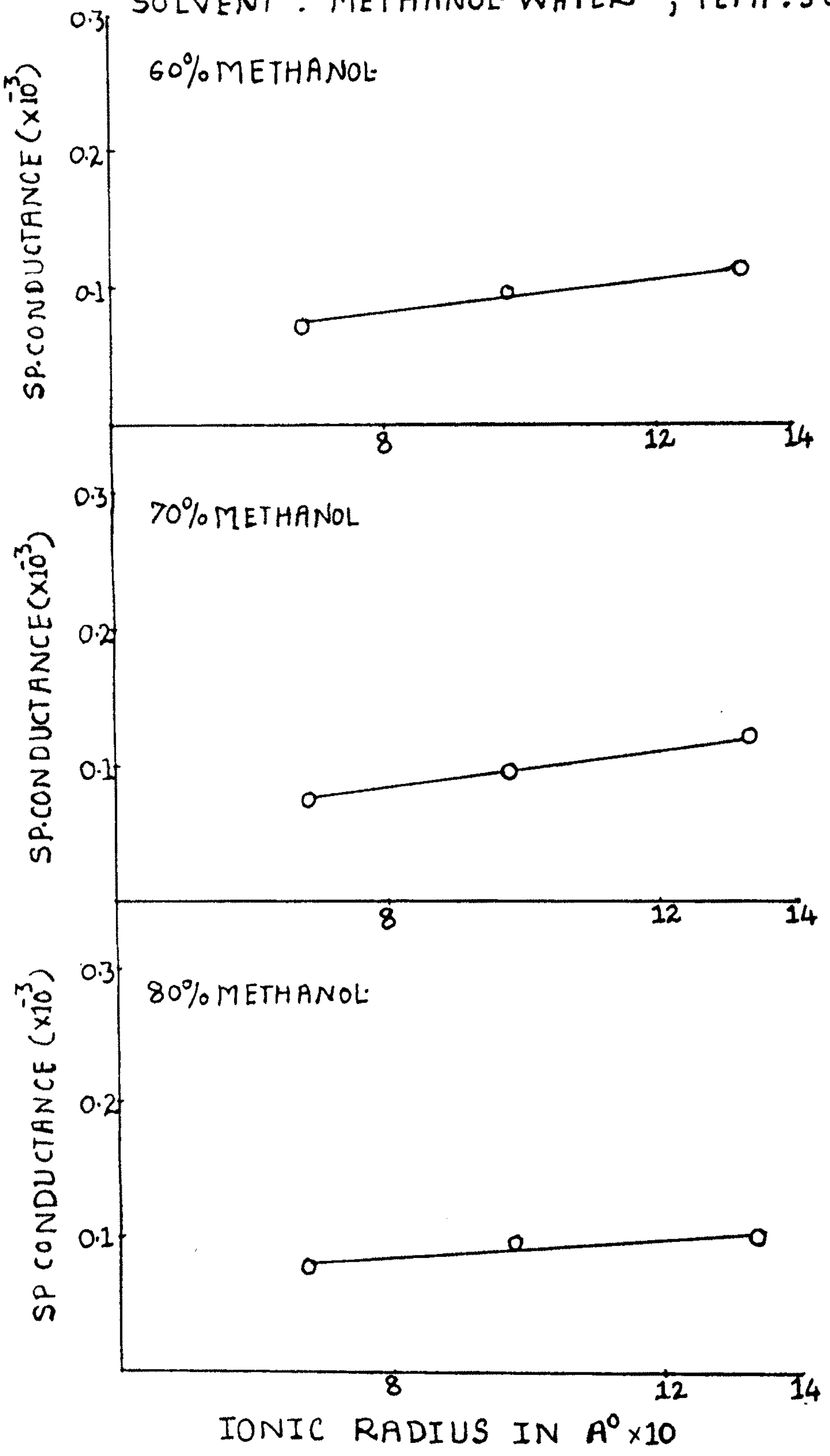


FIG-6.3

SYSTEM : ALKALI METAL SULPHATES [1×10^{-3}M]

SOLVENT: METHANOL-WATER , TEMP: 10°c

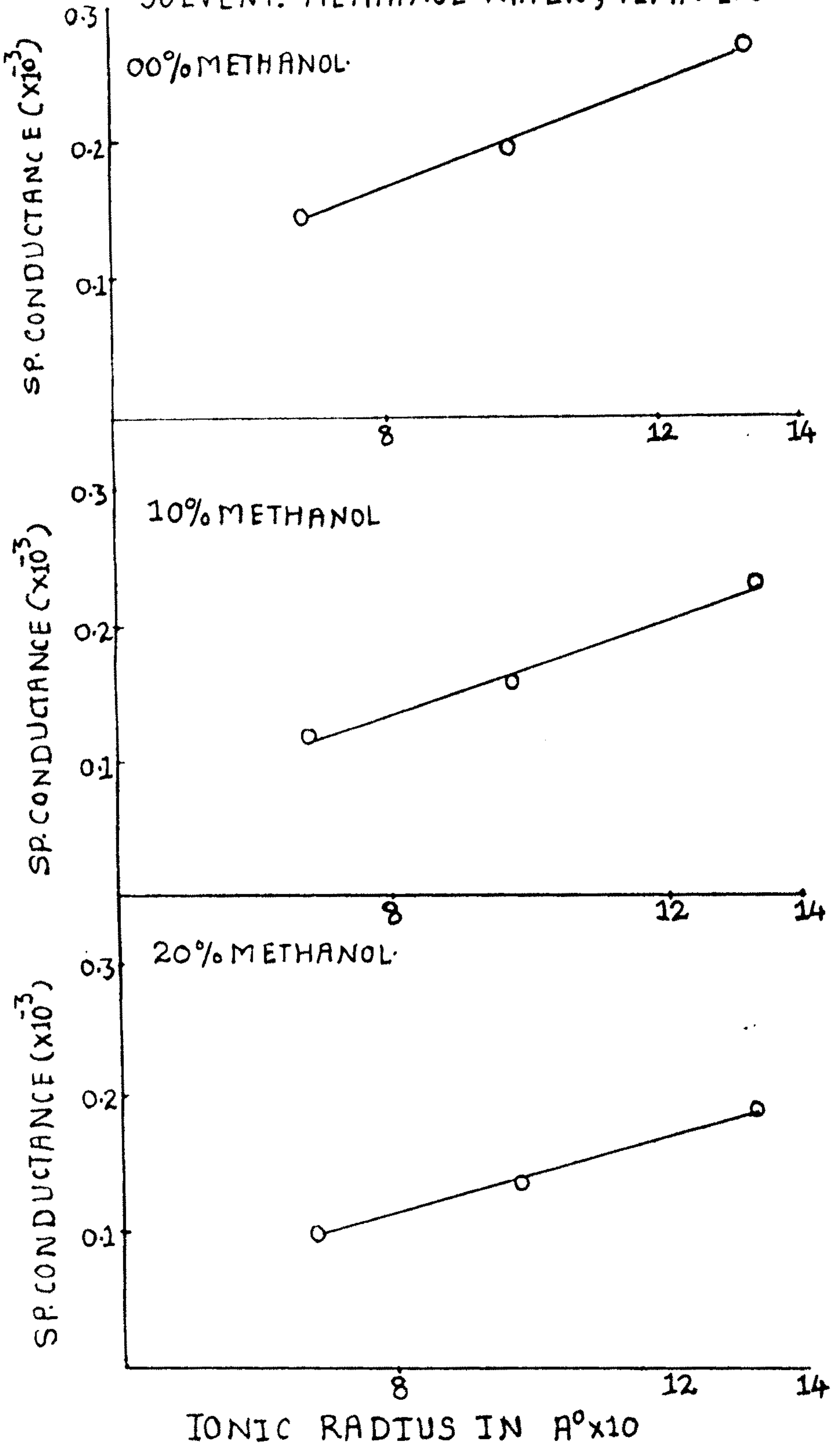


FIG - 6·4

SYSTEM : ALKALI METAL SULPHATES [1×10^{-3} M]

SOLVENT : METHANOL-WATER, TEMP: 10°C

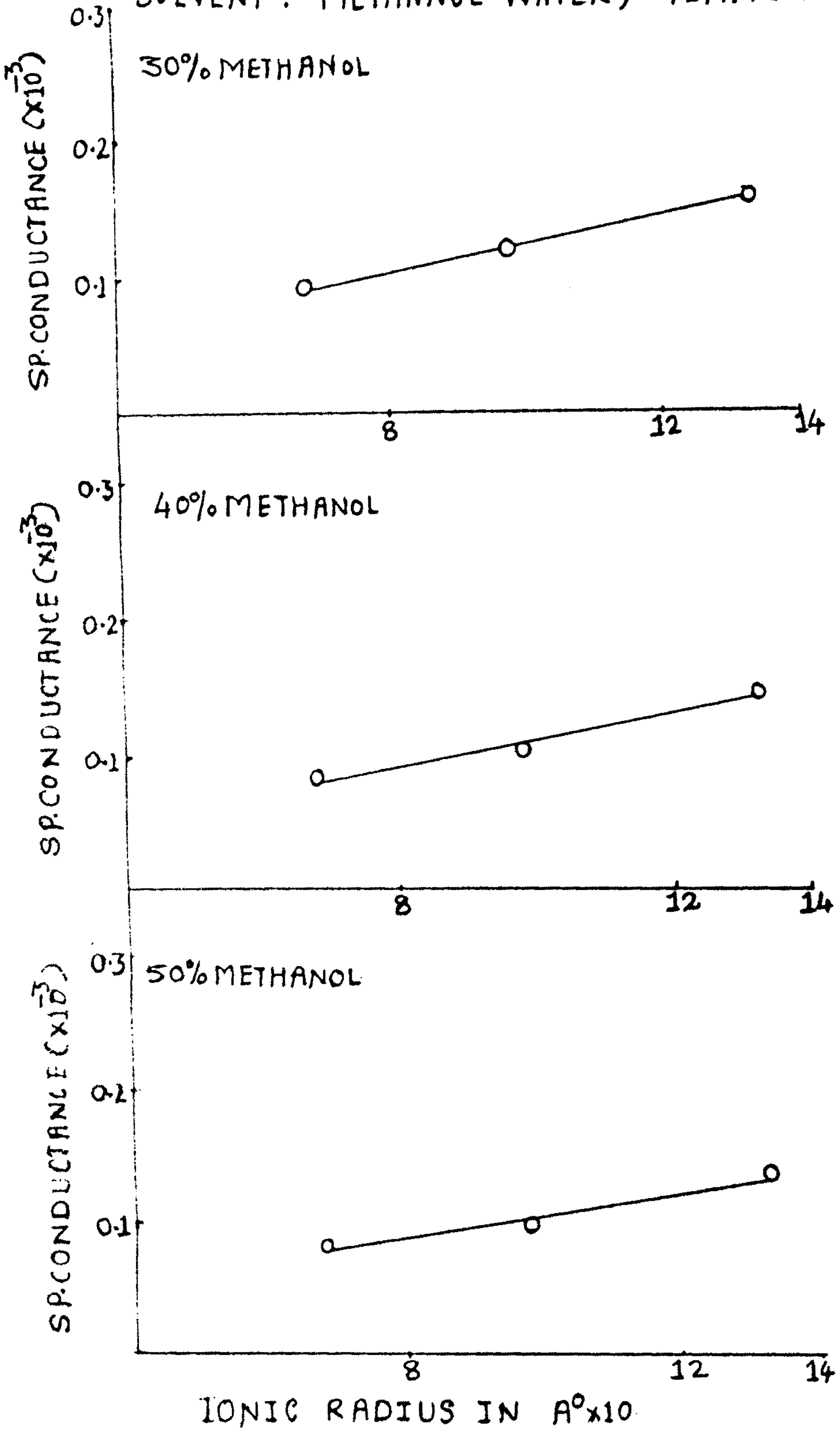


FIG- 6·5

SYSTEM : ALKALI METAL SULPHATES. [1x10^{-3}M]

SOLVENT: METHANOL-WATER, TEMP: 10°C.

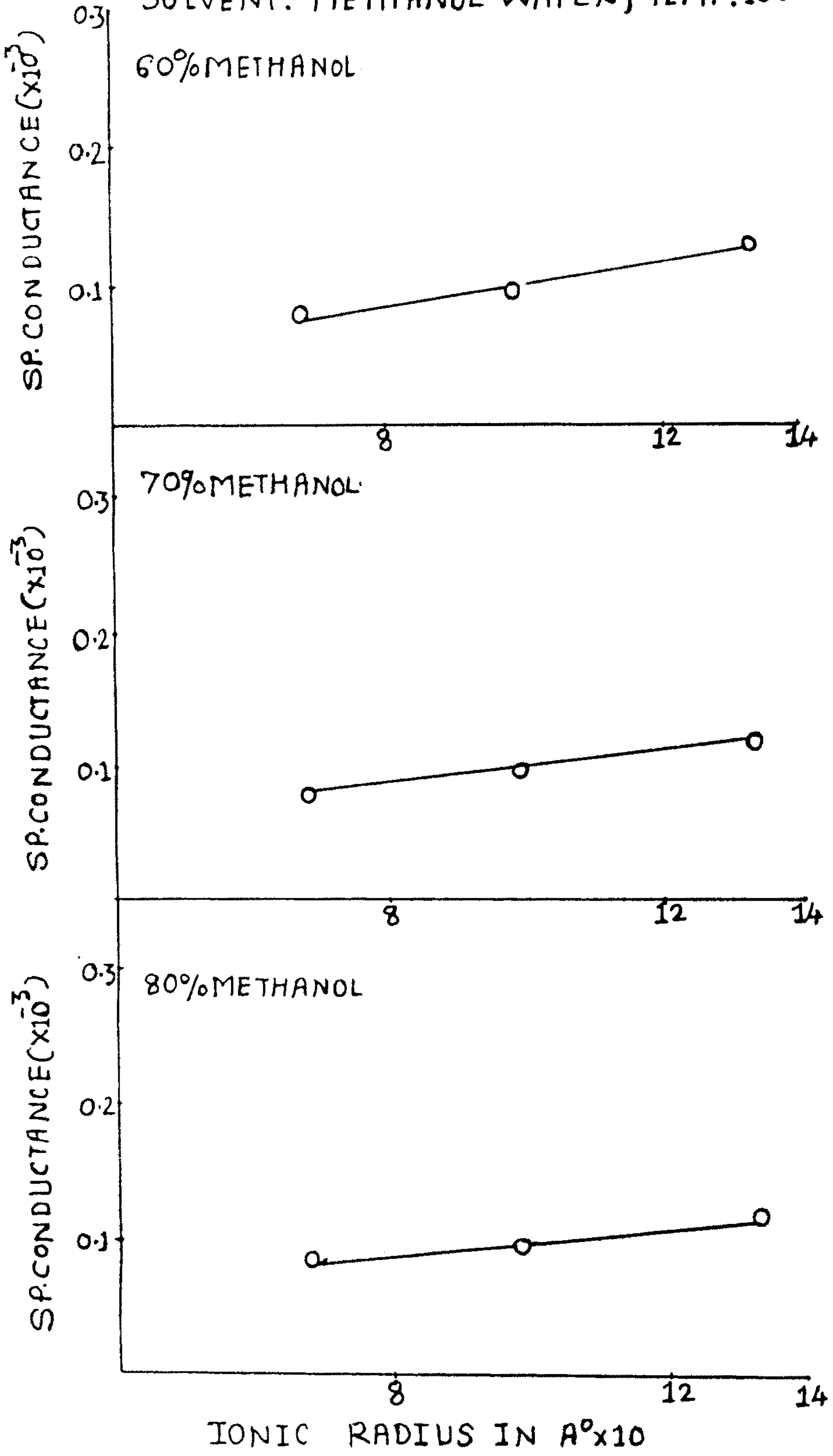


FIG-6-6

SYSTEM : ALKALI METAL SULPHATES [1×10^{-3} M]

SOLVENT: METHANOL-WATER, TEMP: 15°c

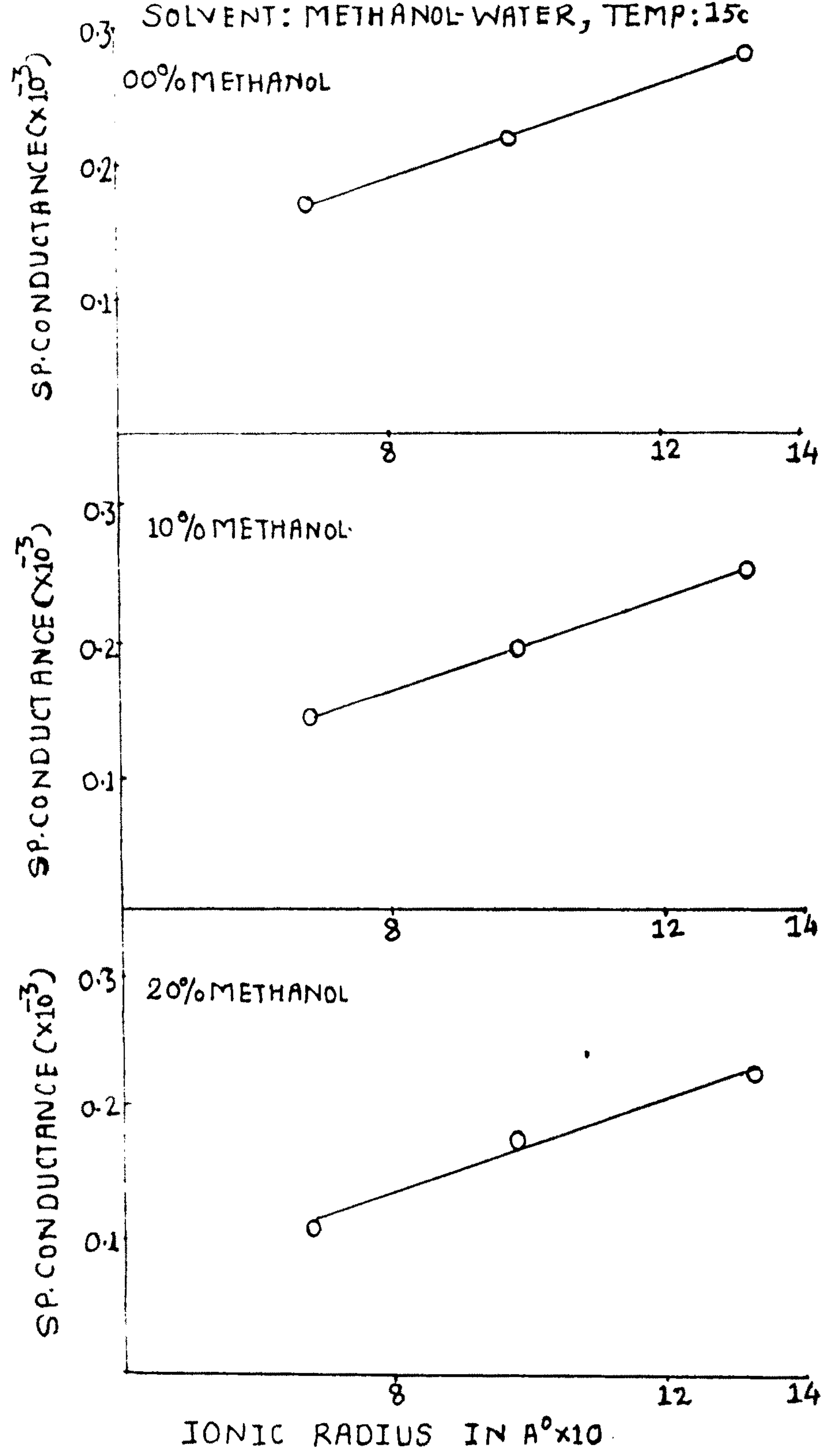


FIG - 6.7

SYSTEM: ALKALI METAL SULPHATES. [1×10^{-3} M]

SOLVENT: METHANOL-WATER, TEMP: 15°c

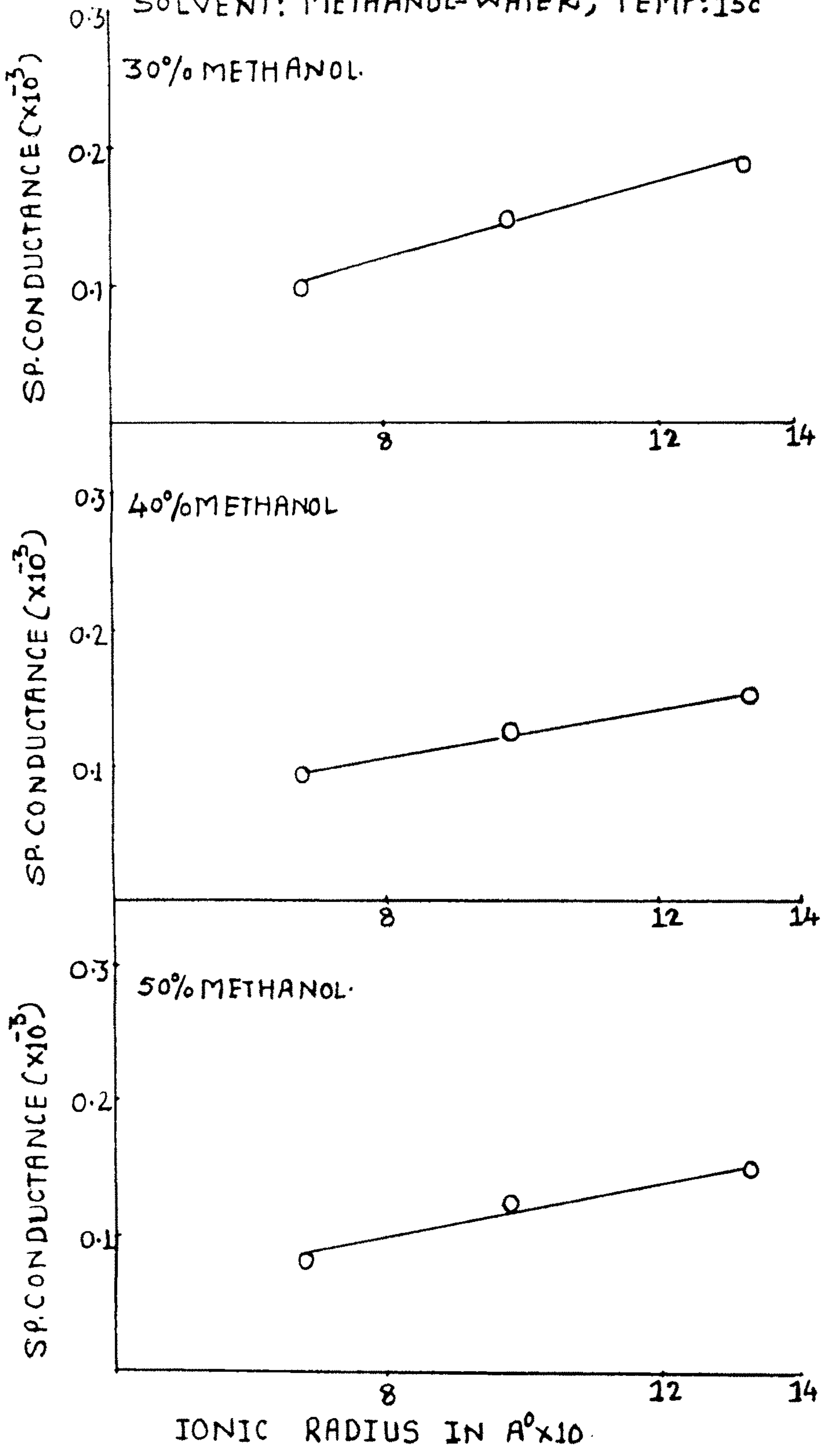


FIG-6.8

SYSTEM : ALKALI METAL SULPHATES. [1×10^{-3} M]

SOLVENT: METHANOL-WATER, TEMP: 15°C.

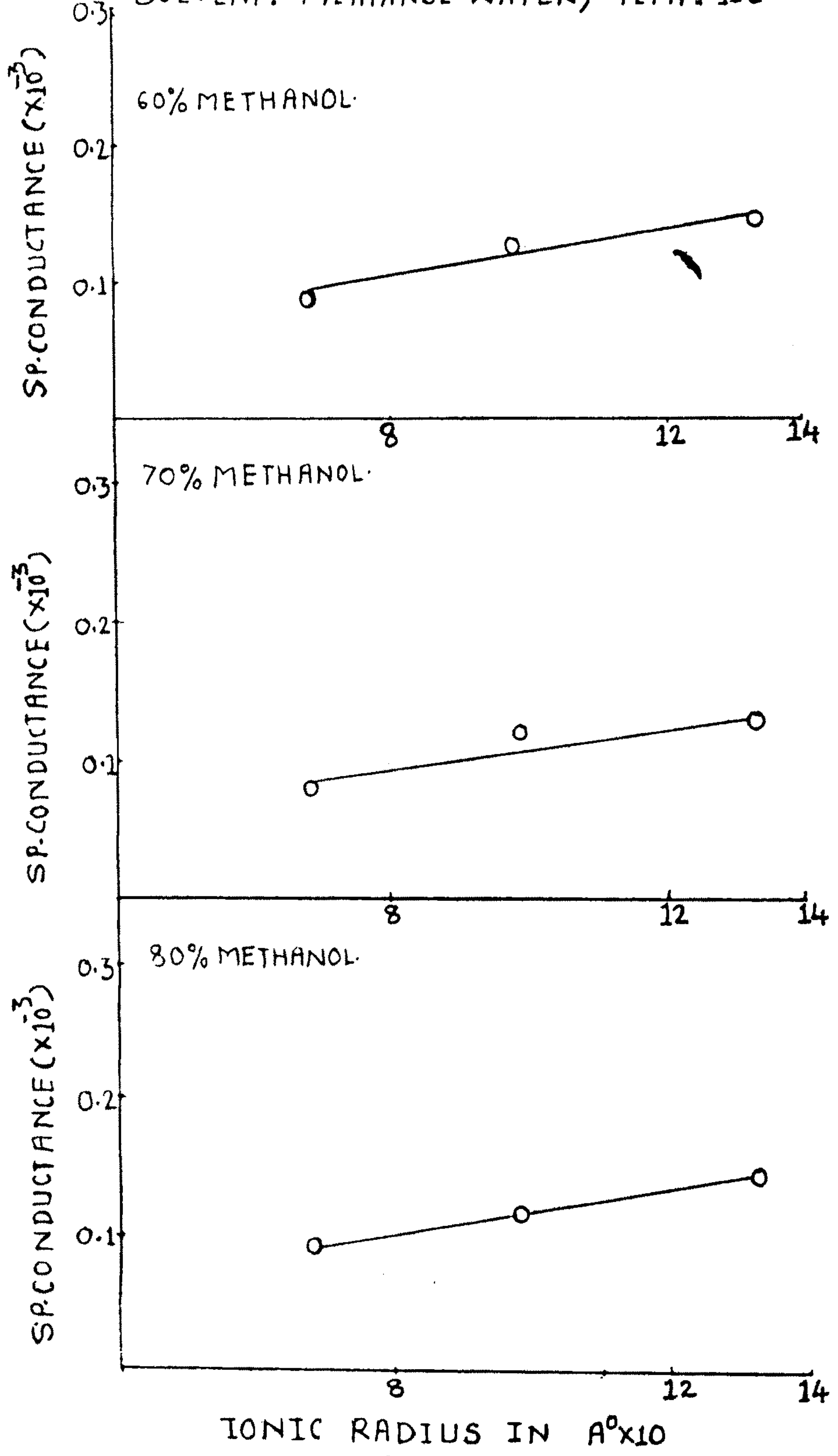


FIG-6.9

SYSTEM: ALKALI METAL SULPHATES. [1×10^{-3}M]

SOLVENT: METHANOL-WATER., TEMP: 20°C

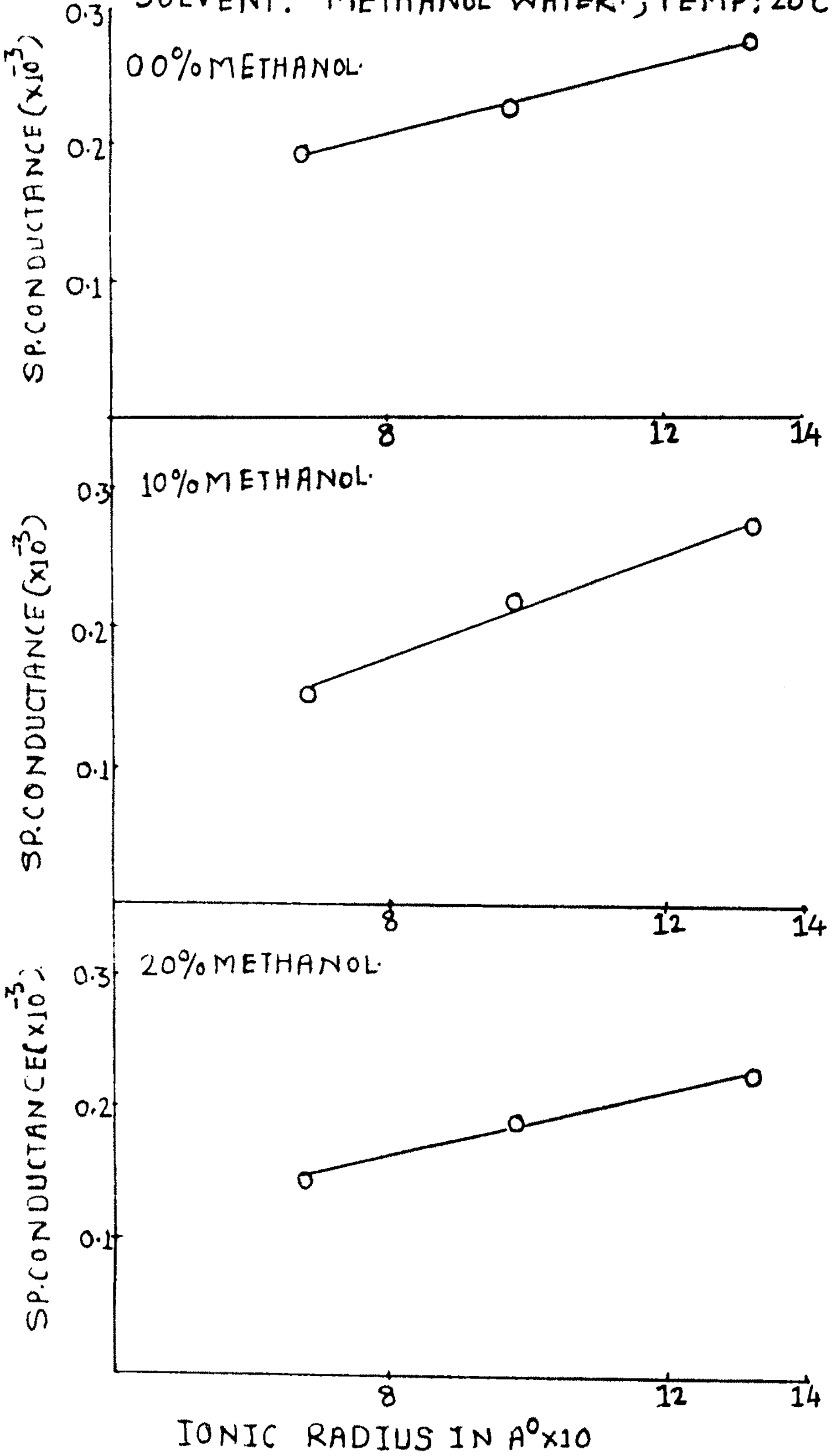


FIG - 6.10

SYSTEM : ALKALI METAL SULPHATES. [1×10^{-3} M]

SOLVENT : METHANOL-WATER, TEMP: 20°C.

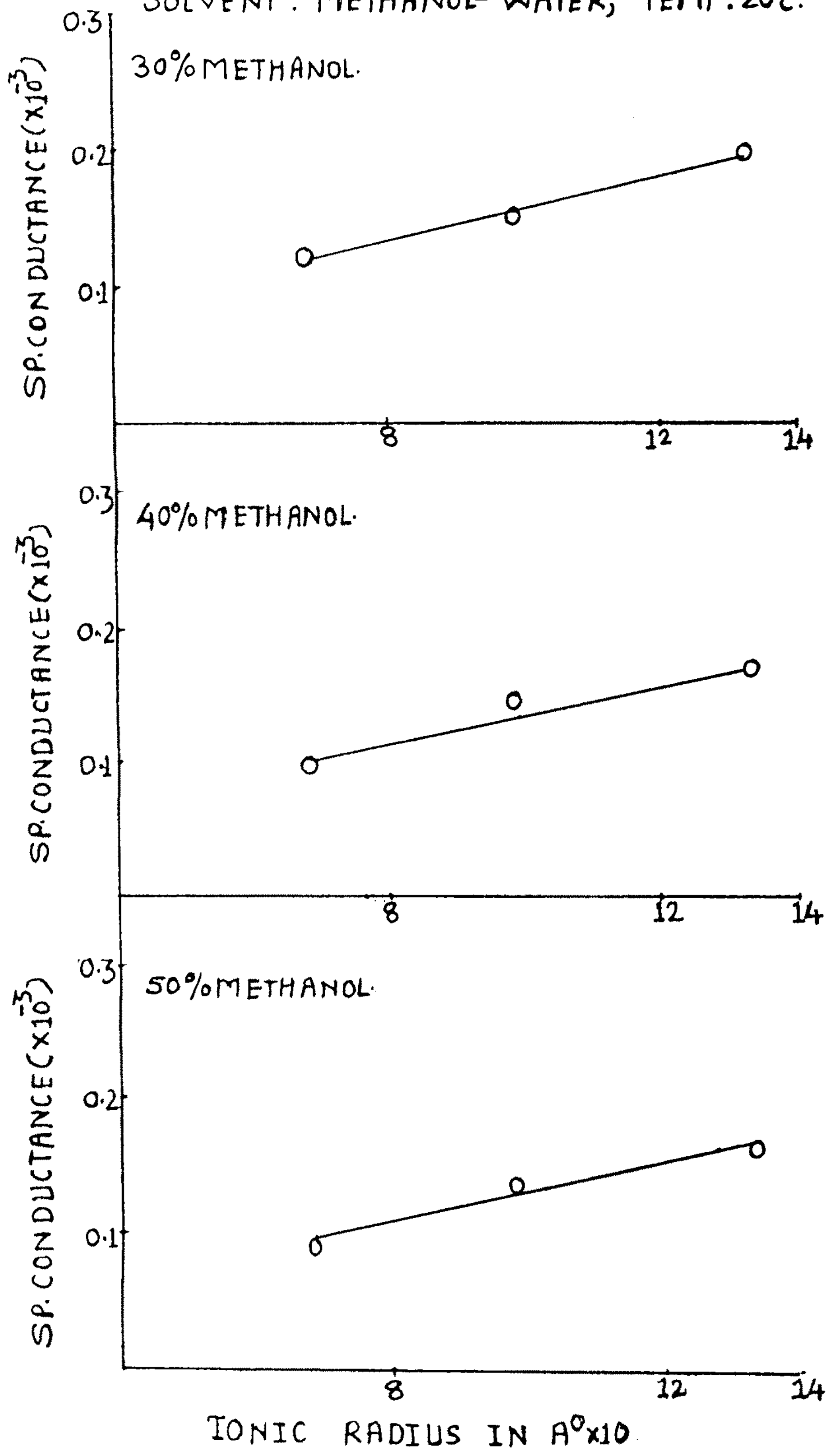
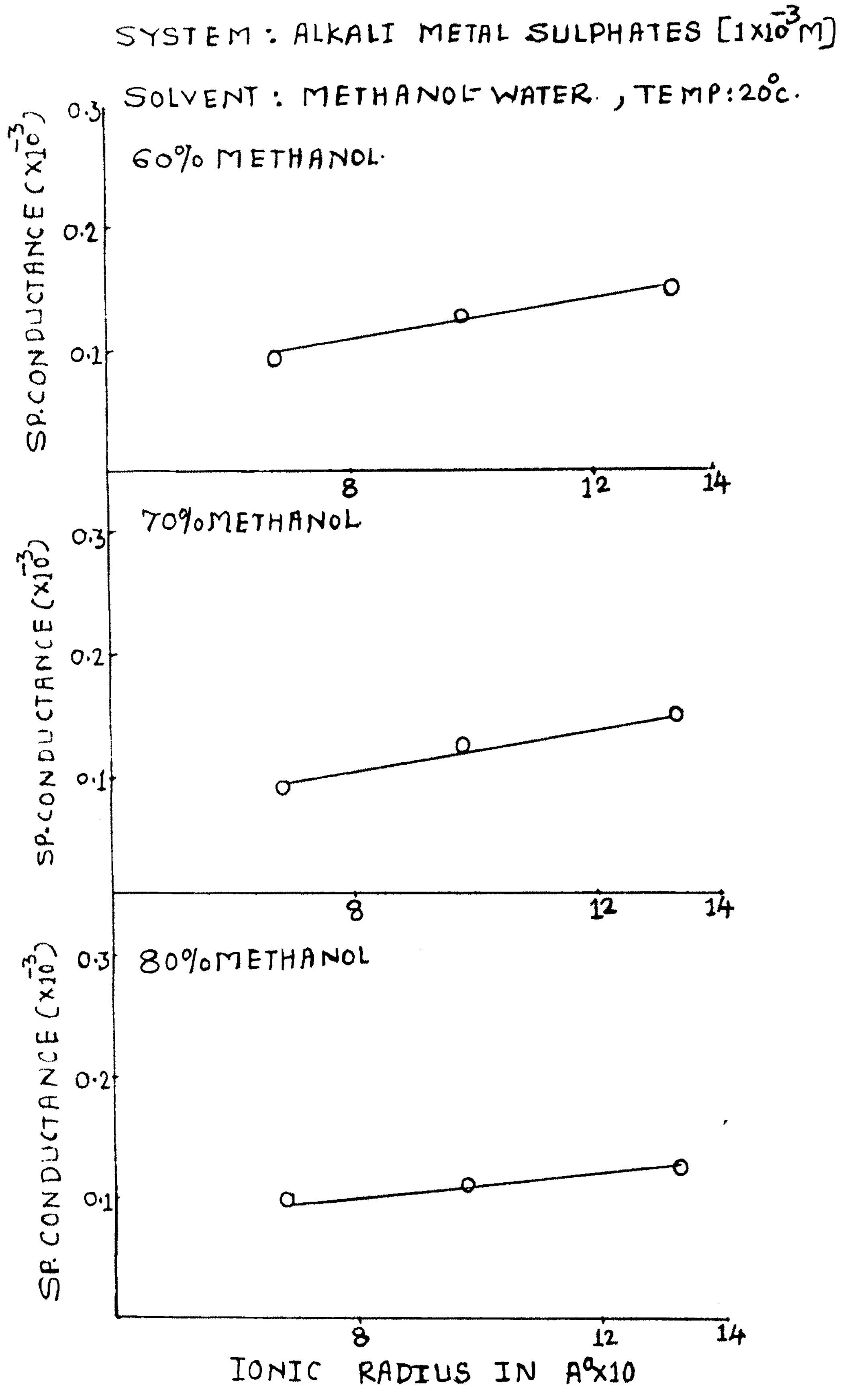


FIG- 6.11


SYSTEM : ALKALI METAL SULPHATES [1×10^{-3} M]

SOLVENT : METHANOL-WATER , TEMP: 20°C.

FIG-6·12

SYSTEM : ALKALI METAL SULPHATES. [1×10^{-3}M]

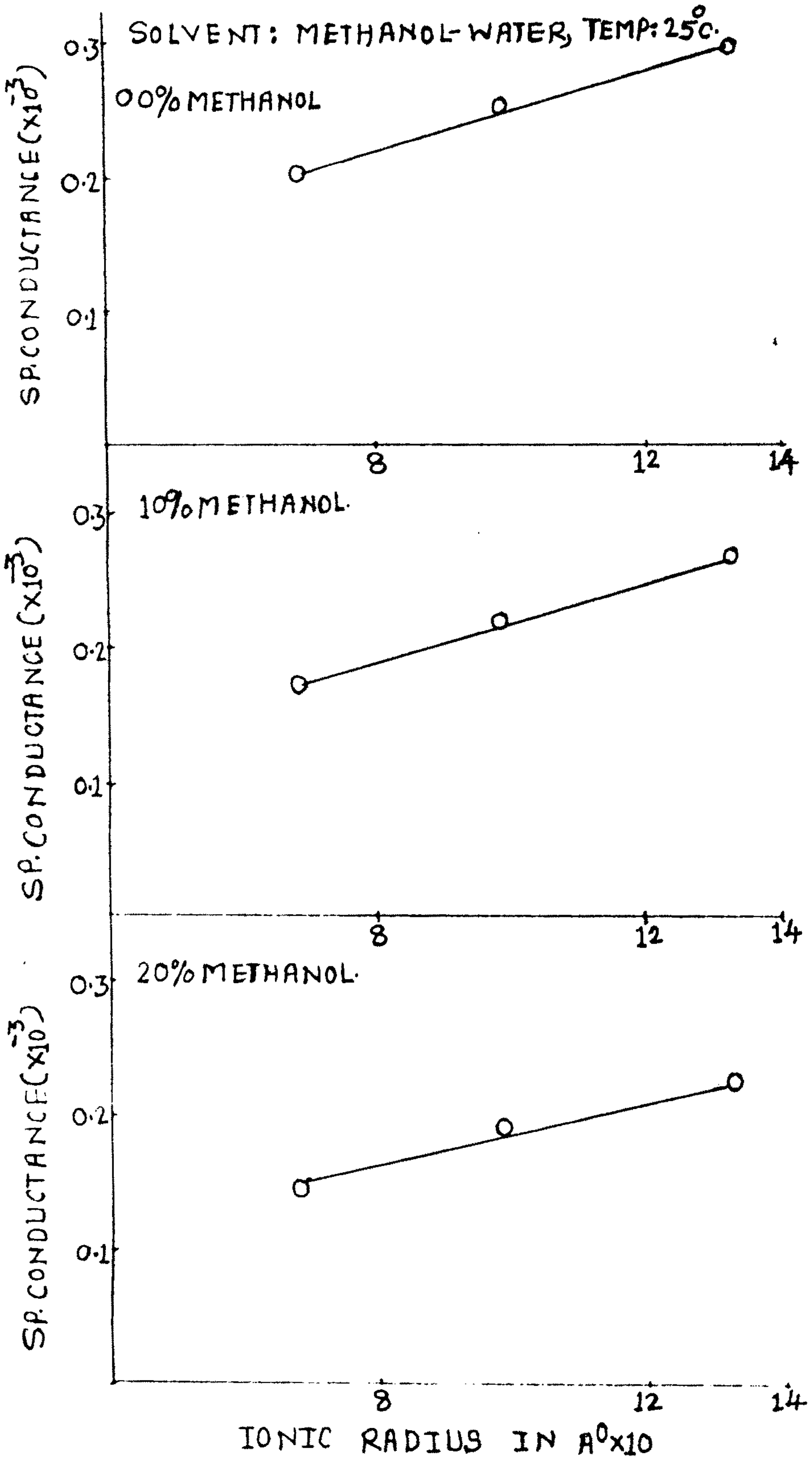


FIG-6.13

SYSTEM : ALKALI METAL SULPHATES. [1×10^{-3} M]

SOLVENT : METHANOL-WATER, TEMP: 25°C

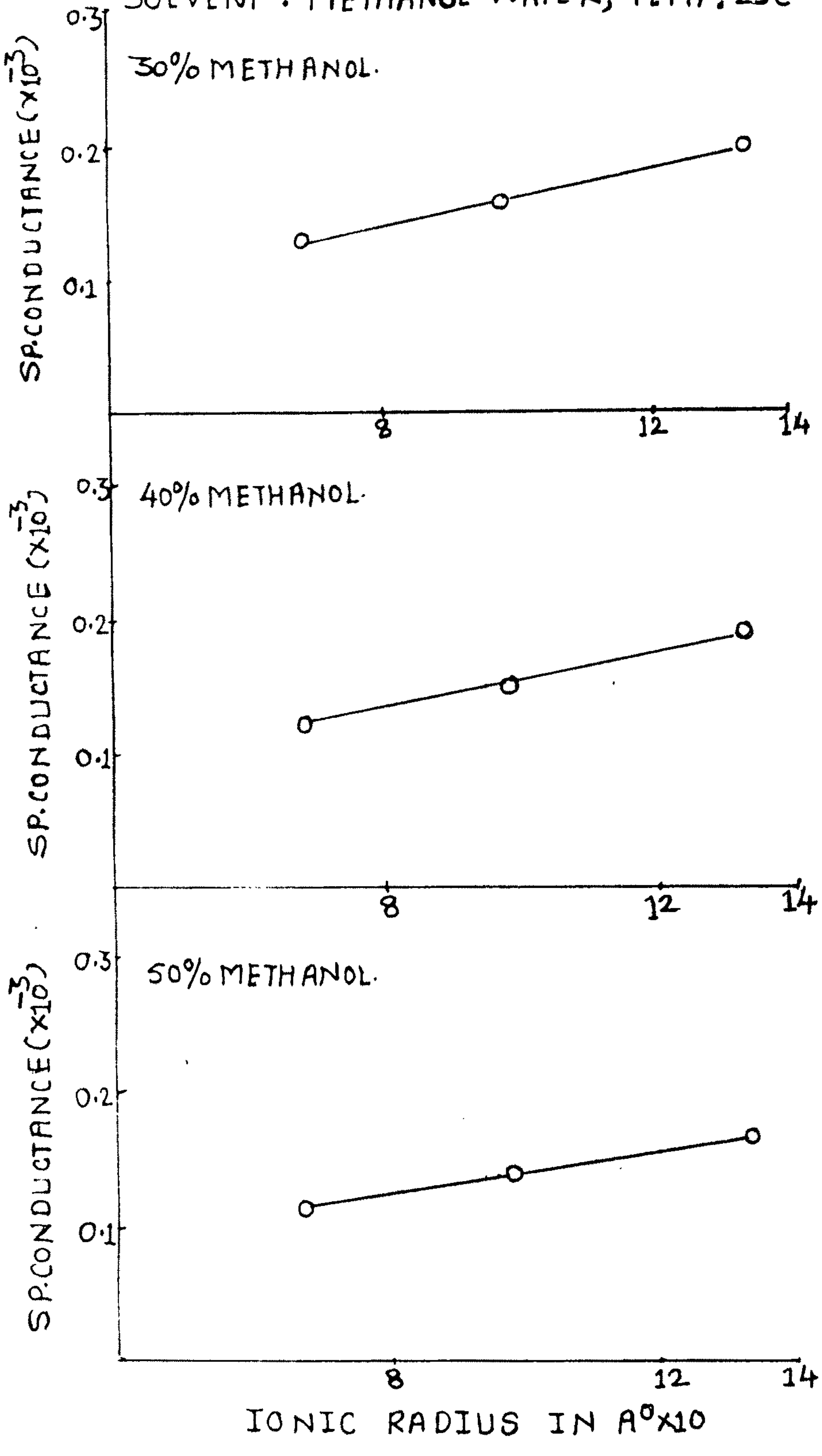
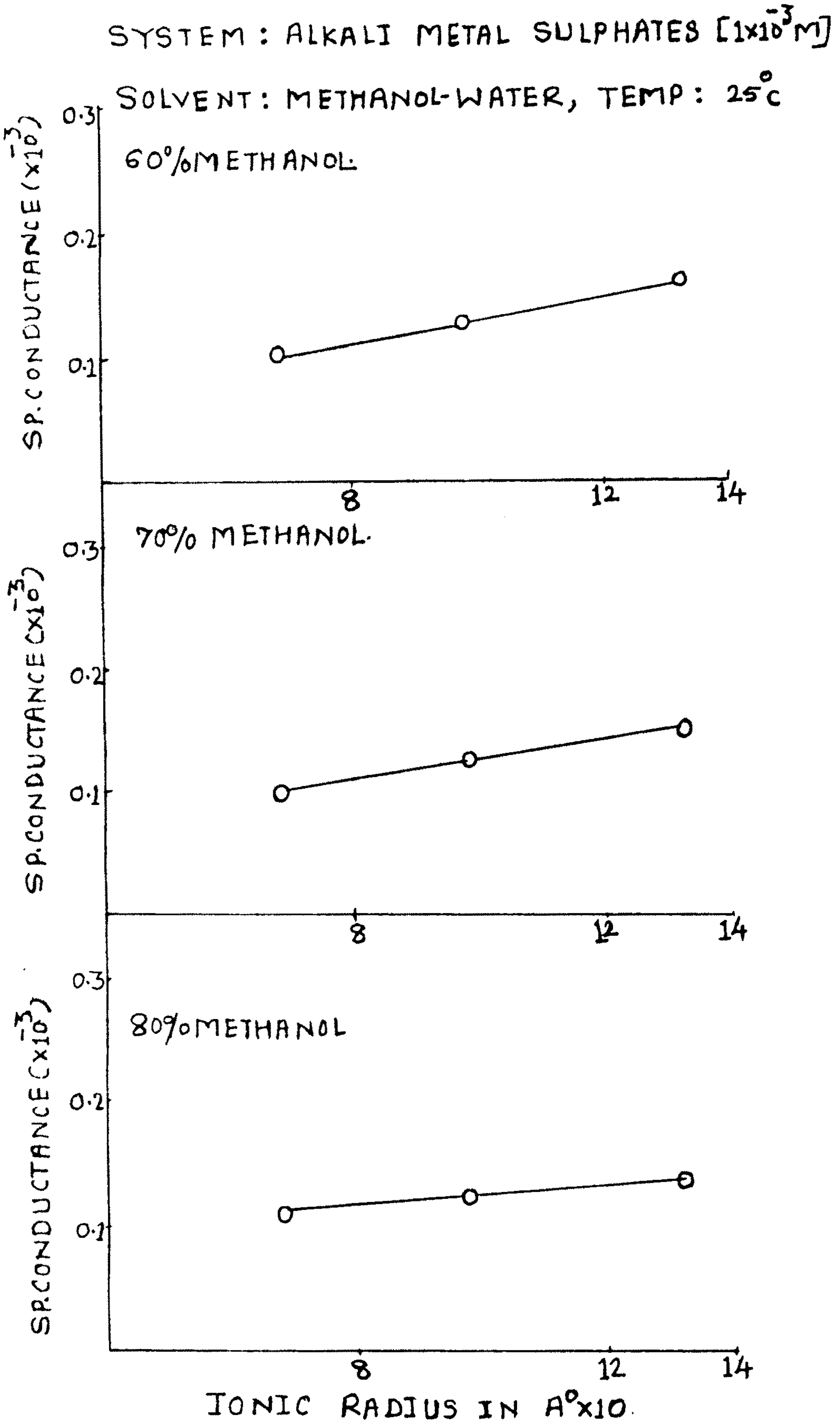


FIG — 6.14


SYSTEM : ALKALI METAL SULPHATES $[1\times10^{-3}M]$

SOLVENT : METHANOL-WATER, TEMP : 25°C

FIG- 6.15

SYSTEM: ALKALI METAL SULPHATES [1×10^{-3}M]

SOLVENT: METHANOL-WATER, TEMP: 30°C

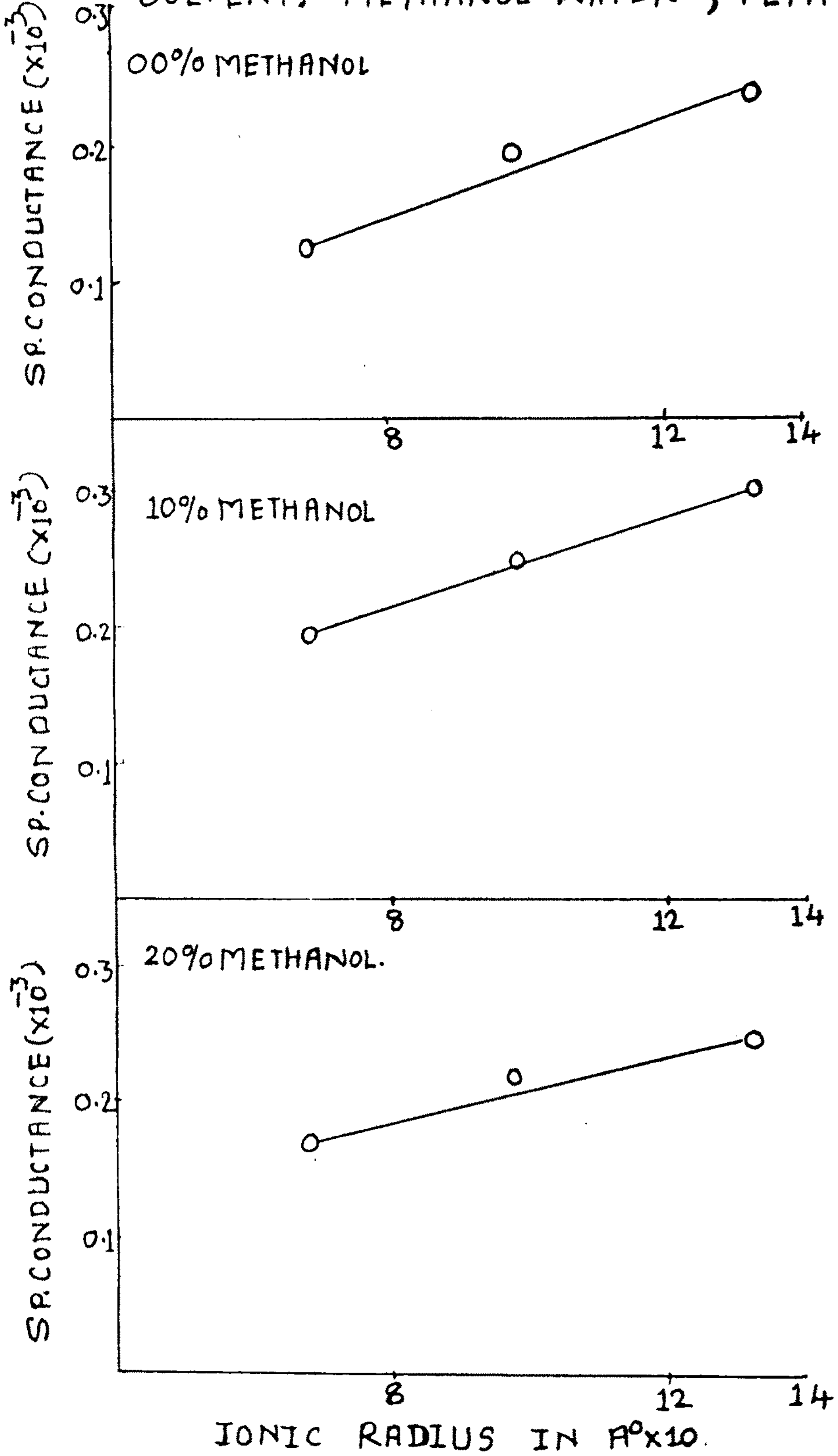


FIG-6.16

SYSTEM : ALKALI METAL SULPHATES [1×10^{-3}M]

SOLVENT: METHANOL-WATER, TEMP: 30°C.

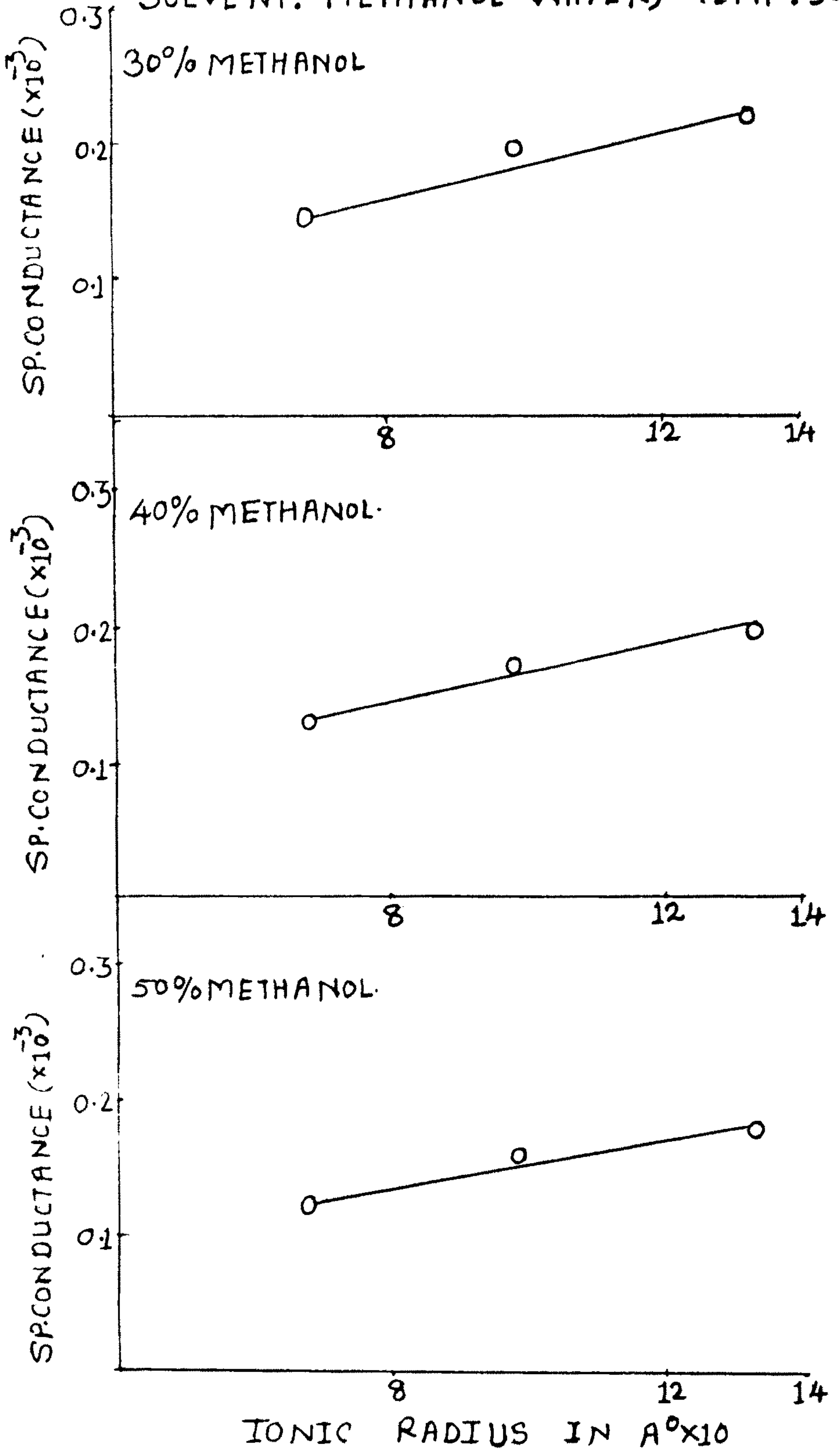


FIG- 6.17

SYSTEM : ALKALI METAL SULPHATES [1×10^{-3} M]

SOLVENT : METHANOL-WATER, TEMP: 30°C.

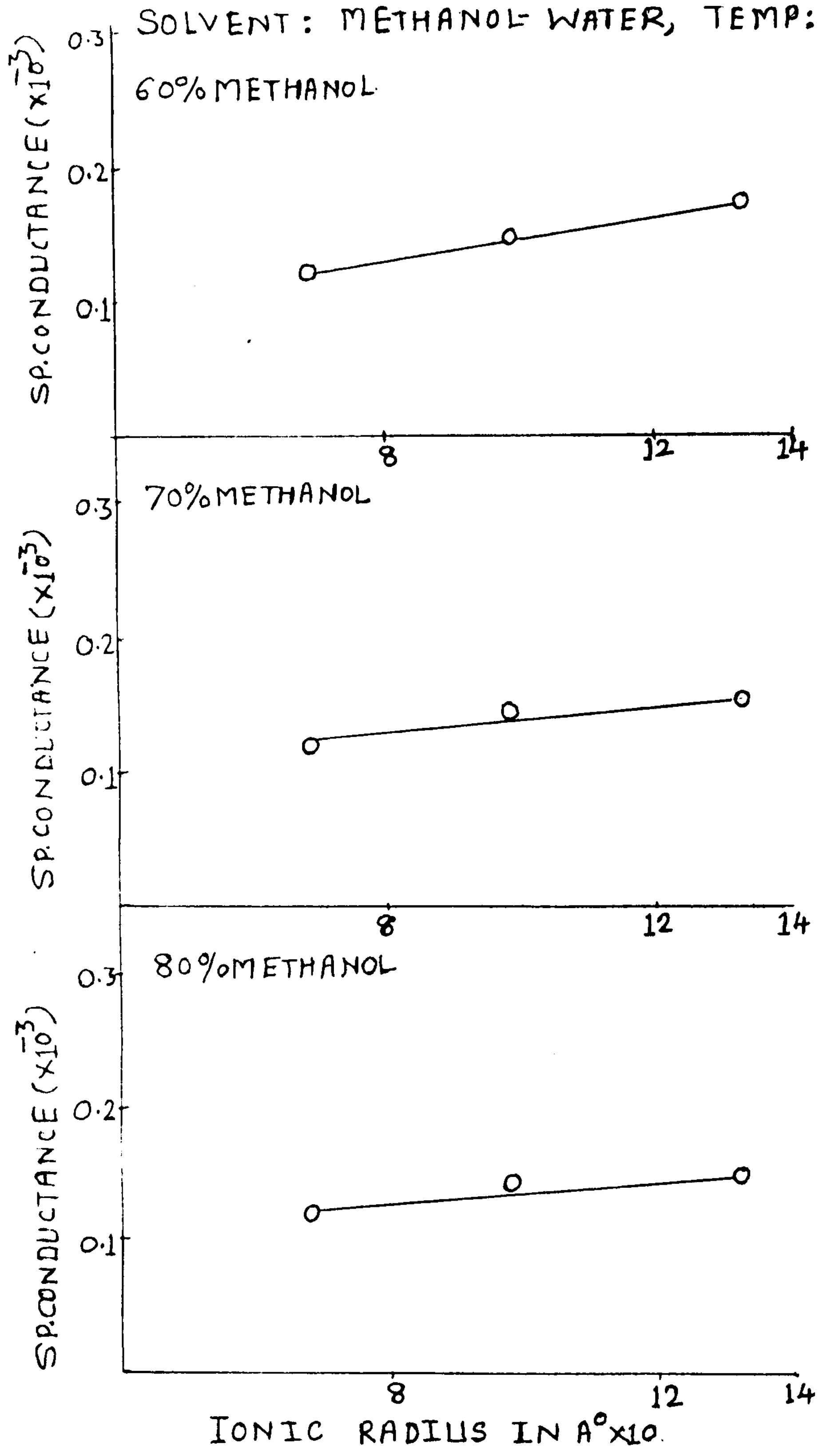


FIG-6.18

SUMMARY

Molar conductivity measurements of the alkali metal sulphates in mixed aqueous solvents such as ethanol-water, methanol-water and acetone-water have been carried out. The composition of the non-aqueous solvents used were 0, 10, 20, 30, 40, 50, 60, 70, 80 and 90%. The conductivity measurements have been carried out at six different temperatures from 5 to 30^{o}c at an interval of 5^{o}c. The concentrations used for ethanol-water were $1x10^{-2}$M, $5x10^{-3}$M, $1x10^{-3}$M, $1x10^{-4}$M, $5x10^{-5}$M $1x10^{-5}$M. For methanol-water the concentrations used were $1x10^{-2}$M $5x10^{-3}$M, $1x10^{-3}$M, $5x10^{-4}$M, $1x10^{-4}$M while for acetone-water, the concentration used were $1x10^{-3}$M, $5x10^{-4}$M, $1x10^{-4}$M, $5x10^{-5}$M, $1x10^{-5}$M.

The results obtained show that the molar conductivity values pass through minimum at lower temperatures 5^{o}c and 10^{o}c for the concentration $1x10^{-4}$M, $5x10^{-5}$M and $1x10^{-5}$M and above these temperatures namely 15, 20, 25, and 30^{o}c there is a regular decrease in molar conductivity with increasing concentration of ethanol. No minimum in molar conductivity has been observed even at low temperatures for the concentration $1x10^{-3}$M and $5x10^{-4}$M.

In the system methanol-water, the molar conductivity values pass through minimum not only at low temperatures but at all the temperatures studied from 5 to 30^{o}c and for the concentrations $1x10^{-2}$M, $5x10^{-3}$M, $1x10^{-3}$M, $5x10^{-4}$M and $1x10^{-4}$M.

In the case of acetone-water system, no minimum in conductivity has been observed at low temperatures 5 and 10^{o}c for the concentrations $1x10^{-3}$M, $5x10^{-4}$M. A rapid decrease in molar

conductivity values have been found beyond 80% of acetone. The behaviour of lithium sulphate, sodium sulphate and potassium sulphate is much interesting at lower concentrations. For the concentrations $1x10^{-4}M$ in acetone-water system, a minimum is obtained at 5 and $10^{o}c$ studied for lithium sulphate while for the sodium sulphate and potassium sulphate there is no minima even at 5 and $10^{o}c$. A minimum in molar conductivity has been observed for the concentration $5x10^{-5}M$ with lithium sulphate, sodium-sulphate and potassium sulphate. A minimum in molar conductance has also been observed for the concentration $1x10^{-5}M$ with sodium sulphate and potassium sulphate.

It has been observed that molar conductivity values of all the three electrolytes in ethanol-water, methanol-water and acetone-water obey the order.

acetone-water $>$ methanol-water $>$ ethanol-water

upto 70% of non aqueous solvent. The order changes beyond 70% as methanol-water $>$ acetone-water $>$ ethanol-water.

Each systems studied at six different temperatures indicate that molar conductivity varies linearly with temperature .

The results of volume contraction indicate that volume contraction is independent of the nature of electrolyte and the concentration of electrolyte. It has been found that volume contraction is constant in the composition range 50 to 70% of non-aqeuous solvents.

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