

INFLUENCE OF ALKALI HALIDES ON ISOPROPANOL/ WATER AND ACETONITRILE / WATER MIXTURES

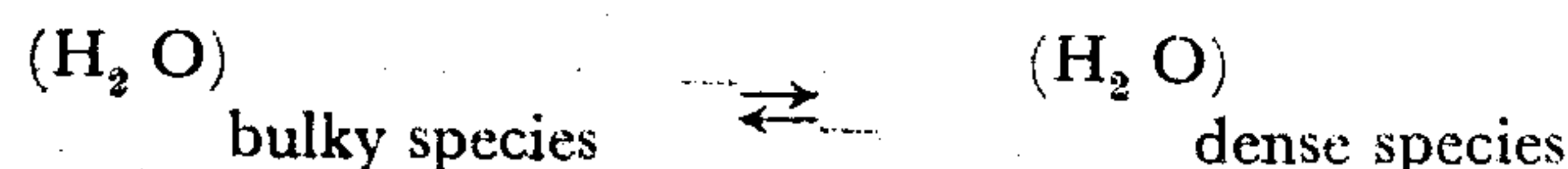
by

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Introduction

The structure of water has been studied extensively for nearly half a century. However as indicated in recent reviews on the subject¹⁻³ no satisfactory picture has yet emerged.

A number of theoretical models have been put forward explaining the structural properties of water. Basically these models could be categorised into four main models according to the nature and number of molecular species encountered in these models. The four models are : Mixture model, Interstitial model, Random network model and Distorted hydrogen bonded model. The Mixture model^{4,5} assumes the structure of water to comprise of a mixture of a small number of distinguishable species of water molecules. The simplest mixture model involves two species to co-exist in the liquid. In most of these two state models the bulky species is considered to be an ice-like cluster of hydrogen bonded molecules, and the dense species is assumed to be more closely packed and could be regarded as non-hydrogen bonded monomers. Properties of the liquid mixture models are then explained in terms of the equation :



The interstitial model^{6,7} is a special class of mixture models in which one species of water molecules is supposed to form a hydrogen bonded framework containing cavities in which the other species, single non-hydrogen bonded water molecules reside. In the distorted hydrogen bonded model⁸ the majority of the hydrogen bonds are regarded as distorted rather than broken and the liquid state of water is considered to be an irregular arrangement of water molecules with distorted hydrogen bonds. The random network model^{9,10} can be considered as an extension of the distorted hydrogen bonded model. Here each water molecule is considered to be hydrogen bonded to four water molecules although the bonds may be considerably distorted.

In contrast to the water structure those of the alcohols seem to be less complicated. In liquid alcohols the oxygen atom of the hydroxyl group through a co-operative effort¹¹ make the molecules extensively hydrogen

bonded to each other. However, the steric effects of the alkyl group restrict the degree of hydrogen bonding and this precludes the three dimensional association. Generally co-association in alcohols through hydrogen bonding leads to linear polymers. However, in the case of higher alcohols Zachariason¹² has shown by X-ray studies that molecules with straight chains are non-randomly associated having the preferred position for the oxygen atoms lying in planes perpendicular to the parallel hydrocarbons.¹³

Many studies have been made on water/alcohol mixtures with a view to understand more about the structure of water. According to Frank and Ives¹¹ alcohols in water have two opposing functions. The pull into solution exerted by the hydrophilic OH group of the alcohol is counteracted by the hydrophobic effect of the alkyl group. Linderström and Vaslow¹⁴ suggested that addition of alcohol to water has a dual effect on the water structure. The alcohol molecules form hydrogen bonds with the surrounding water molecules and it promotes an increase in the order of the adjacent water molecules due to hydrophobic effects of the alkyl groups. This effect is often referred to as the iceberg formation. However, this structural enhancement of water occurs mainly in the region of very low alcohol concentrations. ($X_2 = 0.20$ in MeOH, EtOH, PrⁱOH) in the mixture, as the alcohol molecules at this stage can be incorporated in the 3-dimensional cluster network of water.¹⁵ The enhanced structure thus formed breaks at high alcohol concentrations.

The iceberg formation in alcohol water mixtures was known as a non-electrostatic structure promotion effect and as indicated by Barclay-Butler,¹⁶ the very large negative entropies in these mixtures have been interpreted in terms of immobilization of water in the vicinity of solute molecules where iceberg formation takes place. The structures of icebergs formed in these mixtures are found to be different from that of the ice. According to Kingston and Symons¹⁸ the enforced presence of bulky and near spherical groups (alkyl groups of alcohols) can induce well defined structure in their neighbourhood as in crystalline water clathrates. Pots and Davidson¹⁷ have found a clathrate hydrate of ethanol of the form EtOH · 17 H₂O, (melting point -72°). The OH group of an alcohol in a clathrate hydrate does not participate in significant hydrogen bonding and in the U. V. spectra of n-σ* transition, the intensity was found to be minimum at the sight of a clathrate cage since hydrogen bonding was extensively reduced.

As a result of hydrogen bonding in alcohol water mixtures three types of species could be identified at various mixture compositions. The three species are: water-water, water-alcohol and alcohol-alcohol. N. M. R. studies of alcohol water mixtures¹⁹ have revealed the presence of water-water and water-alcohol associates and the water-water type was found to dominate in mixtures with high water content.

Alcohol water mixtures have also been studied by the use of Charge Transfer to Solvent (C.T.T.S.) spectrum of the iodide ion. The spectrum of the iodide ion yields two bands and the lower energy band $2p_{3/2}-0s_{1/2}$ has been used extensively; to study both solvent-solvent and ion-solvent interactions.¹⁸ The C.T.T.S. study on water-alcohol mixtures has indicated that iodide ion is preferentially solvated in the mixtures and extremely small amounts of alcohol in water enhance the structure of water¹⁹ The effects of added salts (including chlorides) on C T T S. spectrum of I^- in various solvents have been extensively studied and the observations are interpreted in several ways.²⁰ However the salt effects in azeotropic systems have not been investigated before.

Experimental :

Spectra were recorded on a Unicam SP 500 spectrophotometer at a constant temperature of 298° K with a fluctuation of $\pm 0.5K$. A matched pair of cells of 0.1 cm path length was used for all measurements and the absorbance at E_{max} was maintained below 0.9 in each measurement. The E_{max} was obtained by the method of mid-point analysis.

Triply distilled water was used and alkali chlorides (B.D.H.) were recrystallized twice using triply distilled water. The salts were then dried at 120°C for four hours in a vacuum drying apparatus (Gallenkamp). Iodide samples were prepared in the same manner and handling was done in the diffuse light due to their photosensitivity and stored in a dark place. Spectrograde sample of Isopropanol (Hopkins and Williams, spectrosol) was used without purification. The Acetonitrile used was BDH (special for spectroscopy). Water/organic solvent mixtures were prepared by mixing appropriate volumes of solvents. The following stock of the concentration, 4, 1, 10^{-1} , 10^{-2} , 10^{-3} and 10^{-4} were prepared and the intermediate solutions were obtained by diluting these stock solutions with the binary system.

Salt effect in isopropanol-water mixtures

The composition of the three solvent systems selected for the above study is given in Table 1. The system B has azeotropic composition while the systems A and C are on either side of B in the composition scale.

TABLE 1
Composition of isopropanol/Water mixtures

Solvent System	Volume % of water	Volume % of alcohol	Molar fraction alcohol
A	18.0	82.0	0.55
B	12.2	87.8	0.63
C	6.0	94.0	0.81

The effect of chlorides of Li^+ , Na^+ , K^+ and Cs^+ on the isopropanol water azeotrope (system B) was studied within the concentration range of 10^{-4} M to 10^{-1} M.

The observed pattern of behaviour is in keeping with the general trend where the E_{max} being shifted to higher energies with the increase of concentration of the salt in the solvent system¹⁹ (Fig. 1). However, all salts exhibited very mild behaviour with a very little increase in E_{max} initially and this region is then succeeded by a region where the increase in E_{max} was very pronounced. In order to differentiate the two regions the other region of mild increase of E_{max} was named as the 'normal region' and the other region was given the name 'sudden increase region.' Blandamer²⁰ *et al.* also observed similar variations in their investigations of the effect of pressure

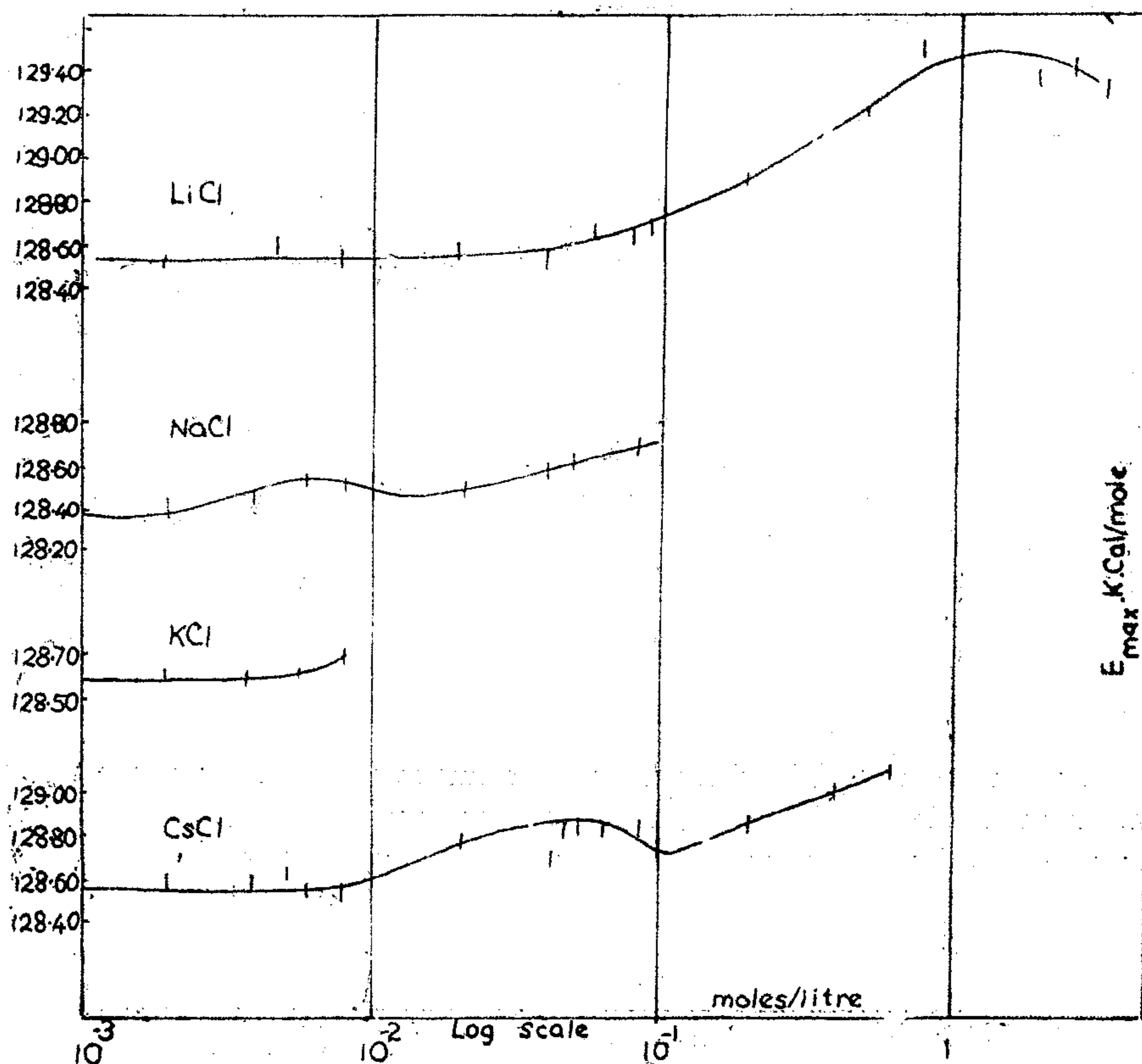


Figure 1 The variation of E_{max}^{25} at different concentration of the chlorides of Li^+ , Na^+ , K^+ , and Cs^+ in the $\text{Pr}^i\text{OH}/\text{H}_2\text{O}$ (82%/18%) system

on the E_{\max} . The extent of the 'normal regions' for each salt varied and there was a gradual decrease in the extent of the 'normal regions' on going from Li^+ to Cs^+ .

The 'sudden increase region' was characterised by the appearance of pronounced humps in the graphs. It is evident from the Fig. (1) that the position of the first hump shifted to low concentration side of the graph in the order, Li^+ to Cs^+ . The first hump of Na^+ is completely hidden and that of K^+ is partly shown. Insolubility of these salts prevented further studies. The graph of CsCl shows a portion of a second hump, in addition a phase separation occurred.

The system (A) had a higher water content than that of the azeotropic system. The solubilities of salts in this system were found to be higher, as could be expected from its high water content and as such investigations were extended over a greater concentration range.

The general trend of the increase of E_{\max} is maintained (Fig. 2). As in the earlier system, the initial normal region was succeeded by the 'sudden increase region' with the increase of salt concentration.

A phase separation was observed in this system with NaCl , at a concentration of 10^{-1}M . Like the CsCl in the earlier system (B) (Fig. 1), a portion of the second hump also appeared in NaCl before phase separation occurred. The phase separation of CsCl in this system was observed at a much higher concentration ($8 \times 10^{-1}\text{M}$) as could be expected from the high solubility of the salt. Thus, the binary system which undergoes phase separation on addition of a salt always showed two humps in the graph before phase separation occurred.

The system (C) had a very low water content compared to the earlier two systems. The studies were confined to the low concentrations (10^{-5}M to 10^{-2}M) as permitted by the solubilities of the salts.

Very low solubility of NaCl and KCl did not permit any investigation. Only the first hump and a small portion of these second hump could be seen

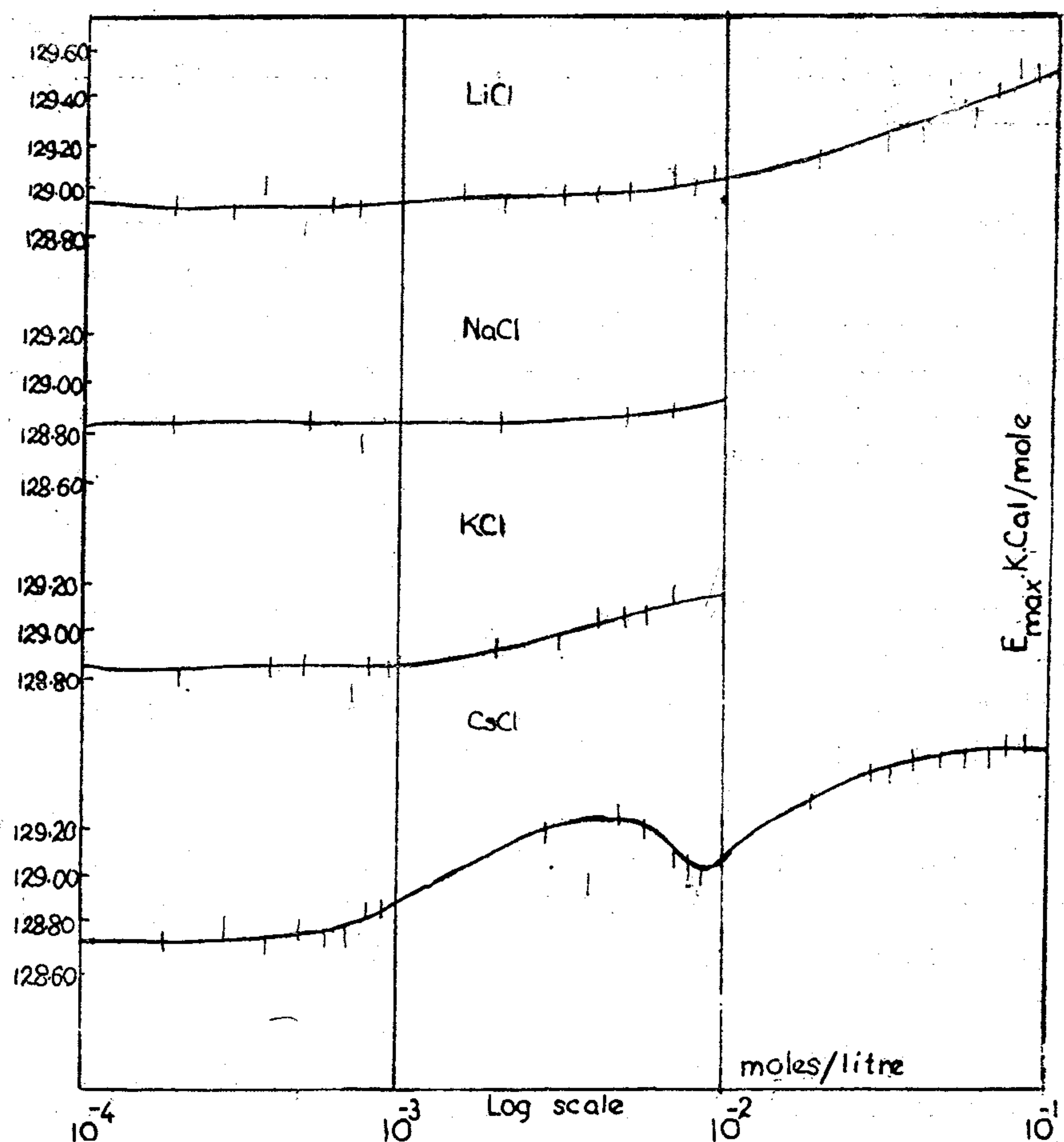


Figure 2 The variation of the E_{\max}^{25} at different concentrations of the chlorides of Li^+ , Na^+ , K^+ and Cs^+ in the $\text{pr}^1\text{OH}/\text{H}_2\text{O}$ azeotropic system.

in the Curves of LiCl and CsCl (fig. 3) and none of these salts gave a phase separation. However, the general trend of the increase of the E_{\max} was observed with the increase of salt concentration.

Salt effects in Acetonitrile-water system

The E_{\max} of I in Acetonitrile (E_{\max}^{20} -116.313)¹⁸ being lower than that of water (E_{\max}^{20} 126.391) binary mixtures similar to the isopropanol/

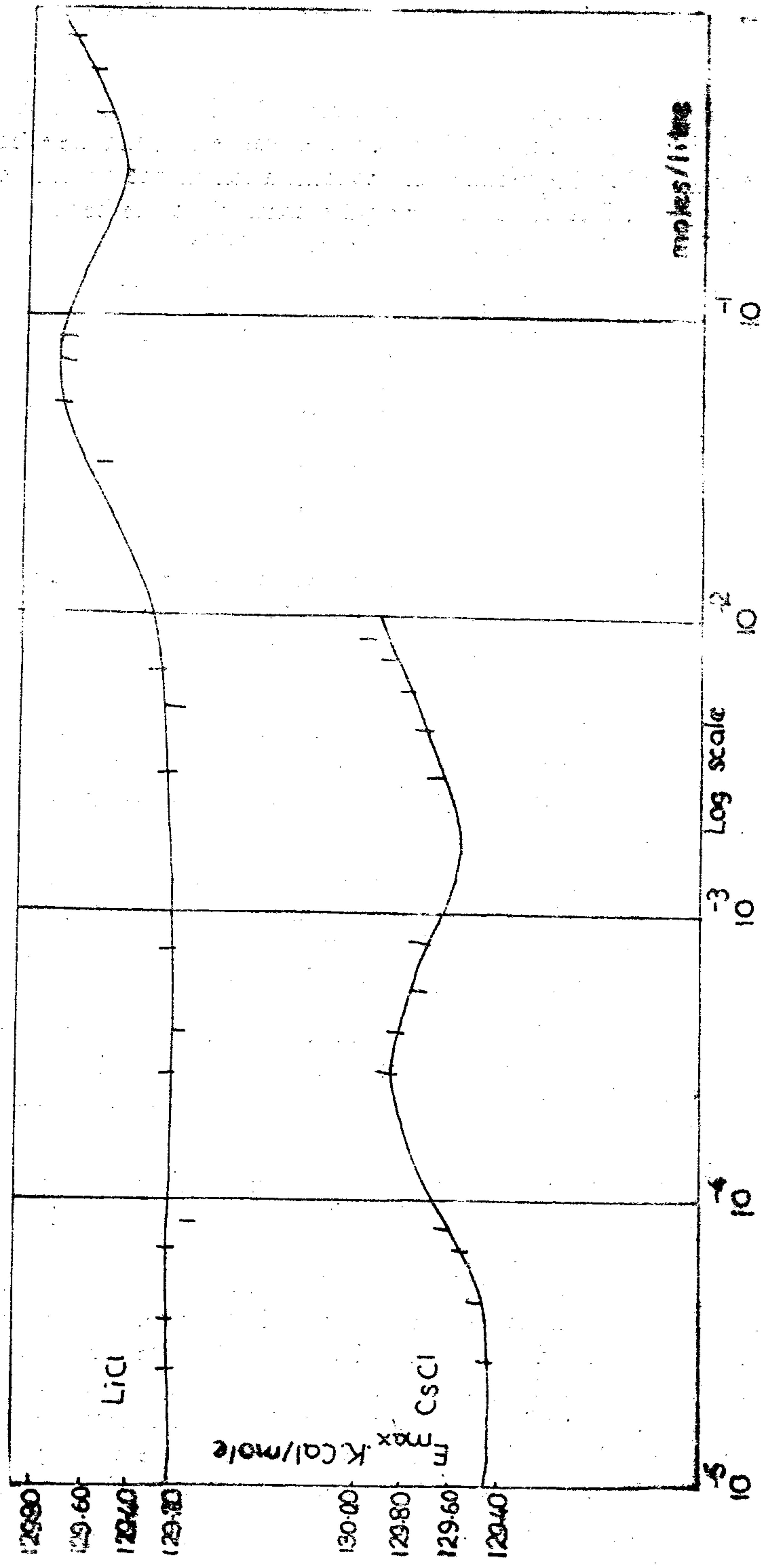


Figure 3 The variation of E_{max}^{25} at different concentrations of the chlorides of Li^+ , Cs^+ in the Pr^iOH/H_2O (94.3/6%) system

water system were studied with a view to substantiate the model proposed to explain the salt effects of isopropanol/water mixture. A solvent mixture with a composition of 90% of acetonitrile and 10% of water was selected and the effect of NaCl on the E_{\max} of iodide within the concentration in the system remarkably shifted E_{\max} of I^- to lower energy quite contrary to the behaviour of alcohol-water system. The E_{\max} values are given in Table 2.

TABLE 2 E_{\max} OF I^- IN ACETONITRILE WATER-(90%—10%)
System at different concentration of NaCl

Concentration of NaCl Mole./Lit	$E_{\max}^{23.5}$ K cal./Mole
5×10^{-4}	124.80
5×10^{-3}	124.70
3×10^{-2}	121.44
5×10^{-1}	120.75

As evident from Table 2 the E_{\max} of I^- approaches a value closer to that pure acetonitrile with the increase of salt concentration. High concentrations of both NaCl and CsCl resulted in phase separations in a mixture with 85% acetonitrile.

The high energy shift of E_{\max} for I^- in all three systems with the increase of salt concentration is in agreement with reported behaviour^{18,19} However the appearance of two peaks in the E_{\max} Vs concentration graphs is remarkable (Figs. 1 and 2).

The behaviour of E_{\max} in the "normal region" is very much similar to that of the initial increases of the E_{\max} with applied external pressure in system of I^- in pure solvents²⁰. The pressure effect has been attributed to initial structural changes of solvents under slight increment of pressure.

Although the behaviour of E_{\max} with added chlorides has a parallel effect, the initial structural changes as suggested by Griffiths and Wijayanayake¹⁰ seem to be a secondary effect where the influence of added salts is concerned.

The added salt will undergo solvation in the mixture and the cations will take up water in preference to alcohol and this effect is more pronounced with alkali metal cations. As reported by Gauz²¹ the monomeric water present in alcohol water mixtures can easily attract alkali metal cations. Thus the added salt will take up monomeric water initially, and as the salt concentration is increased water associated to alcohol and lastly to I^- will be taken up¹⁹. Hence the gradual increase of E_{\max} observed in the 'normal region' could be attributed to a dehydrating effect for which the cation is solely responsible. This dehydrating effect is felt by the I^- ion in its solvation sphere causing the E_{\max} to shift more towards the value of alcohol with increase of salt indicating that the I^- is now surrounded by alcohol.

The validity of this dehydration concept could be seen in the acetonitrile/water system. In this system the addition of salt shifts the E_{\max} to lower energies as opposed to that observed in the isopropanol/water mixtures. The shift to lower energies is brought about by the removal of water molecules by the added salt resulting in an enhancement of the solvation of I^- ions by the acetonitrile, Hence E_{\max} should shift towards the acetonitrile value as observed in Fig. (4).

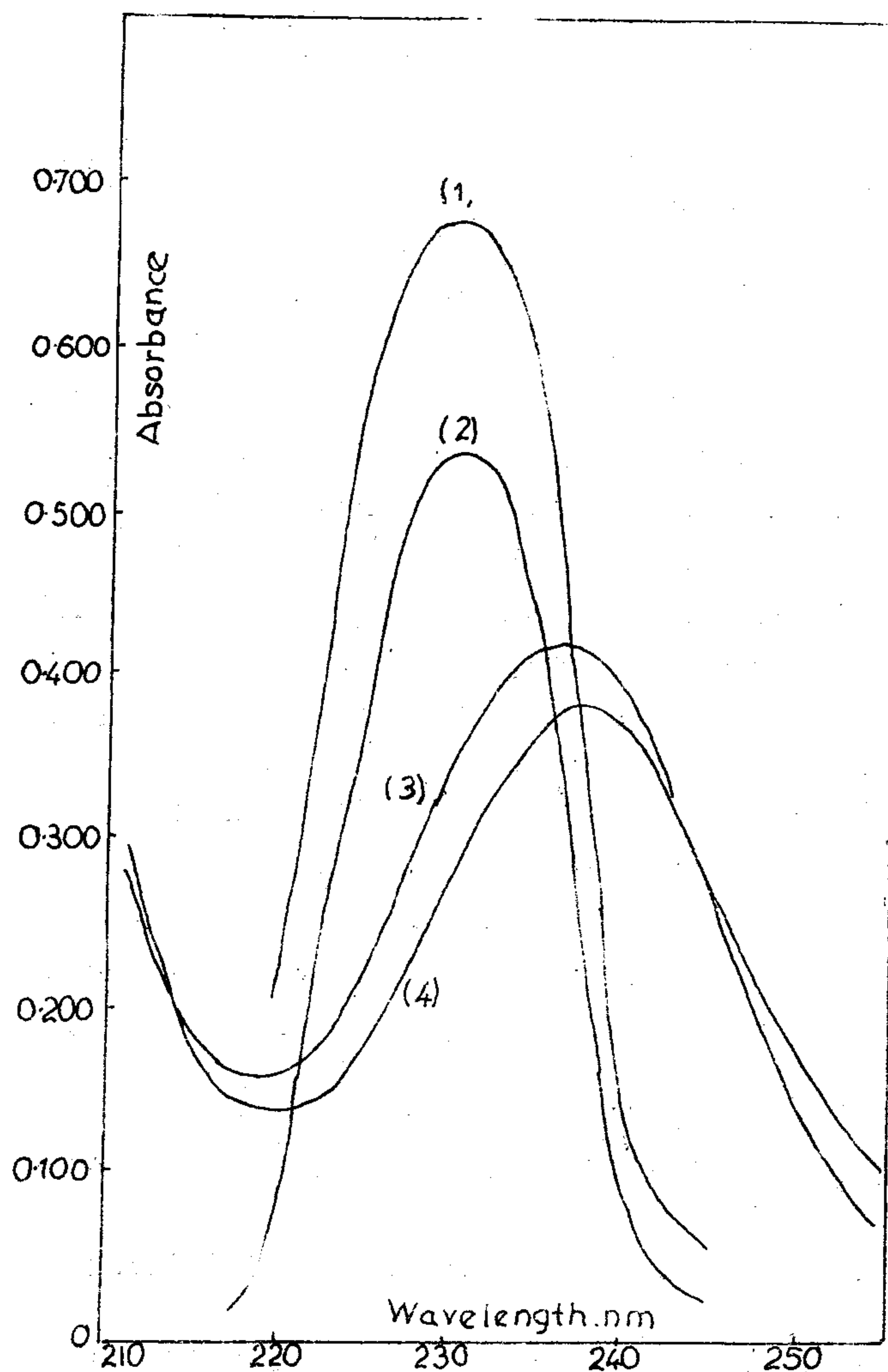


Figure 4 The shift of $E_{\max}^{23.5}$ to lower energies with the increase of concentration of NaCl in acetonitrile-water (90%/10%) system. The concentration increases in the order (1) < (2) < (3) < (4).

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