SPECTROSCOPIC AND THERMOELECTRIC VAPOR PHASE OSMOMETRIC STUDIES OF ALKALI AND AMMONIUM ION SOLVATION IN NONAQUEOUS SOLVENTS

Thesis for the Degree of Ph. D.
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MING KEONG WONG
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This is to certify that the

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AND AMMONIUM ION SOLVATION IN
NONAQUEOUS SOLVENTS

presented by

Ming Keong Wong

**has been accepted towards fulfillment
of the requirements for**

Ph. D. **degree in** Chemistry

Alexander I Popov
Major professor

Date July 29, 1971

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ABSTRACT

SPECTROSCOPIC AND THERMOELECTRIC VAPOR PHASE OSMOMETRIC STUDIES OF ALKALI AND AMMONIUM ION SOLVATION IN NONAQUEOUS SOLVENTS

By

Ming Keong Wong

The techniques of infrared, Raman, and nuclear magnetic resonance spectroscopies as well as thermoelectric vapor phase osmometry have been combined to study the solutions of alkali metal and ammonium salts in acetone, acetic acid, tetrahydrofuran and mixed solvent systems.

In acetone, solutions of a given cation show new far infrared bands which can be ascribed to an alkali ion vibrating in a solvent cage. For solutions of lithium salts, the far infrared bands are anion-independent for the polyatomic anions, but anion-dependent for the halides, e.g., the bands occur at 423, 412, and 409 cm^{-1} for the iodide, bromide and chloride, respectively. The anions chloride and bromide are shown to have a stronger affinity for the cation than the acetone molecule. The anion-dependent far infrared bands may arise from the vibration of solvated contact ion pair or the vibration of the cation in a cage formed by the anion and near neighbor solvent molecules. The anion-independent far infrared bands arise from the cation vibrating in a solvent cage.

In an attempt to determine the lithium ion coordination number in acetone, mole ratio studies were carried out in nitromethane.

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The absorption intensity of the far infrared band, the shifting of the Raman perchlorate band and the nmr proton shift of acetone were followed as a function of the acetone/lithium mole ratio. The results indicate that the lithium ion is solvated by four acetone molecules.

In acetic acid, new far infrared bands are also observed for lithium salts and some of the metal fluorides. All of the lithium salts used showed a band at 390 cm^{-1} whose frequency was independent of the nature of the anion. A band was observed at 280 cm^{-1} for the alkali and the tetramethylammonium fluorides. No cation-dependent bands were observed at lower frequencies ($<$ 150 cm^{-1}) for the heavy alkali ions. It is concluded that due to its hydrogen-bonding ability, acetic acid solvates the fluoride ion. On the other hand, it is a poor solvating agent for the cations and only the lithium ion, which has a stronger tendency for solvation than other alkali metal ions, shows the solvation band in acetic acid.

Thermoelectric vapor phase osmometric measurements of the alkali metal salts in acetone and tetrahydrofuran solutions indicate that in some cases aggregates higher than ion pair exist in these solvents. The degrees of aggregation of the electrolytes are higher in tetrahydrofuran solutions. Among the electrolytes studied, lithium chloride is the most highly aggregated in both solvents.

Nmr proton chemical shift studies of solvent mixture systems of acetone, acetic acid, dimethyl sulfoxide and nitromethane indicate that dimethyl sulfoxide is the strongest donor solvent, while nitromethane is the weakest. The donor strengths of acetone and acetic acid are approximately equal.

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By

Ming Keong Wong

A THESIS

Submitted to
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in partial fulfillment of the requirements
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Department of Chemistry

1971

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Deep appreciation is extended to my wife, Irene, for her love, understanding and encouragement during the course of this study. Last, but not least, special mention is extended by my daughter, Ting Yean, who always so cheerfully saw "daddy" off to work in the laboratory regardless of whether it was a cold, snowy winter night, or a hot, muggy summer evening.

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I. INTRODUCTION

The importance of ion-solvent and ion-ion interactions in solutions of electrolytes is exemplified by hundreds of publications in this field. Yet at this time these interactions are understood only in rather crude qualitative terms. The knowledge of the various types of species that are present in electrolyte solution, the equilibria between these species as well as the influence of the solvent properties on the nature of these species and equilibria is quite limited.

When an electrolyte is dissolved in a solvent, four general types of interactions occur: ion-ion, ion-dipole, dipole-dipole, and hydrogen-bonding. These interactions result in the formation of many different types of solvated species. The identification and the characterization of these solvated species present a major challenge in solution chemistry. The difficulty lies in differentiating among solvated ions, solvated ion pairs and higher aggregates.

If the species is a solvated ion, characterization of the solvation sphere is difficult, e.g., depending on the investigation method, vastly different solvation numbers for the same system have been reported in the literature. If the solvated species is an ion pair, discerning the nature of the ion pair itself is another major problem. Several different types of ion pairs may be present. For the present purpose, three distinct species will be considered: (1) contact ion pair, in which an anion and

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cation are in direct contact; (2) solvent-shared ion pair, in which one solvent molecule separates the two ions; (3) solvent-separated ion pair, in which each ion is solvated individually and yet retains an attraction for the other. The characterization of these three different ion pairs by various measurement techniques has been pursued by this research group for a number of years, and the present work is part of this larger study.

The detection and characterization of aggregates higher than ion pair in solution is also a major problem, especially for low polarity solvents, in which higher aggregates are known to exist extensively. For this purpose, vapor phase osmometry is introduced in an attempt to study the degree of aggregation of the various electrolytes in the solvents used in this study.

Extensive experimental data for various electrolyte solution systems are needed in order to elucidate the nature of the various species present, and thus be able to postulate their behavior and the equilibria between them. In previous studies conducted in this laboratory, the solvents dialkylsulfoxides (1) and pyrrolidones (2) were examined. These solvents are highly polar and have good donor properties. It is well known that the nature of the solvents play an important role in determining the properties of the electrolyte solutions. However, not much is known on the influence of solvent on the various solvated species and their equilibria. Thus it is of interest to examine the electrolyte solution system in solvents with divergent properties. The work presented in this thesis is an extension of the aforementioned studies in solvents with medium and low polarities: acetone, acetic acid, and tetrahydrofur

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tetrahydrofuran. A qualitative comparison of the donor strengths of some of the solvents studied thus far is also performed.

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II. HISTORICAL SECTION

Spectroscopic Studies of Ionic Solvation

Ion-solvent interactions in electrolyte solutions have been extensively studied for many decades. Yet until now these interactions are still vaguely understood and can be discussed only in qualitative terms. During the past decade it became evident that the far infrared, Raman and nuclear magnetic resonance techniques can be very useful in the elucidation of the structure of electrolyte solutions (1-27). A more extensive historical discussion of solvation studies can be found in the Ph. D. theses of Brian W. Maxey (1) and John L. Wuepper (2) of Michigan State University.

In the far infrared measurements of alkali metal and ammonium salts, a band was observed which could not be assigned to the solvent or the solute and whose frequency was dependent on the mass of the cation. In polar solvents such as dimethyl sulfoxide (1) and 1-methyl-2-pyrrolidone (2) or in solvents with strong donor ability, such as pyridine (8), the frequency of the band, with very few exceptions, was independent of the nature or the mass of the anion. In a nonpolar solvent, such as tetrahydrofuran (9, 10), the band frequencies were anion dependent. It has been postulated that in the first case the bands were due to the vibration of the cation in the solvent cage, while in the latter,

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the bands were probably due to either the vibration of an unsolvated ion pair or the cation vibrating in a cage which contains the anion of the salt. Ion pair vibrations of tetraalkylammonium salts were also observed in benzene solutions (11).

Most Raman spectroscopic studies in solutions have been carried out on the aqueous electrolyte systems (14-19). A Raman study of electrolytes in methanol showed that the anions are more influential in affecting O-H bonds than are cations (20). Most of the far infrared solvation bands reported thus far were shown to be Raman inactive, indicative of electrostatic bonding between the cation and the solvent. A Raman band at 202 cm^{-1}, ascribed to ion motion of sodium tetrabutylaluminate ($NaAlBu_4$) in cyclohexane has been recently reported (13).

In recent years, proton magnetic resonance has been widely used for the study of aqueous and nonaqueous electrolyte solutions. A more extensive discussion of such studies can be found in the Ph. D. thesis of John L. Wuepper (2). Most of these studies involve the measurement of the proton chemical shifts of the solvent. A few studies have been reported on ^7Li and ^{23}Na chemical shifts in aqueous and nonaqueous solutions of electrolytes (21-25).

Acetone

Acetone is one of the most common nonaqueous solvents. Many organic and inorganic compounds are readily soluble in acetone. The solvent has wide liquid rance (-95.4° to 56.2°C), a moderate dielectric constant of 20.76 at 25° (28), and a Trouton constant of 21.5, indicating that it is a relatively unassociated liquid. The solvent has intermediate solvating power, and according to mann's scheme (

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Gutmann's scheme (29), it has a donor number of 17.

The acetonate of sodium iodide, $NaI \cdot 3CH_3COCH_3$, is well known due to its use in a method for the purification of acetone (30). The solid diacetonate of lithium bromide has been prepared by Bell, et al. (31). It was found to decompose into the unsolvated salt and acetone at 35.5°C.

Electrical conductance studies of alkali, ammonium and tetraalkylammonium salts in acetone have been plentiful (32-45). The ion pair dissociation constants for the various salts obtained from such measurements are tabulated in Table 1. In cases where several studies on the same salt have been reported, the agreement among the various values is rather poor. Examples of reported ion pair dissociation constants of lithium bromide and potassium iodide in acetone are shown in Table 2. The discrepancies, besides experimental error, can be attributed to the difference in the method of data treatment, and to the purity of the solvent and the salts. In such cases, the most recent values are listed.

The dissociation constants show that in acetone, as would be expected for a solvent with a dielectric constant of 20.76, dissolved electrolytes are mostly undissociated. Adams and Laidler (36) in a series of papers on mass transport of tetraalkylammonium salts in acetone, have rationalized the results with the assumption of at least two species of ion pairs, "solvent-separated" and "solvent-shared" ion pairs. The presence of contact ion pairs was postulated in solvents of lower dielectric constant.

Beronius, et al. (47) studied the ion pair reactivity of lithium bromide in acetone by kinetically measuring the exchange of ^{82}Br between the salt and butyl bromide. Their study showed

Table 1. Diss

Compoun
LiCl
LiBr
LiI
$LiClO_4$
LiPi
Li p-toluenes
NaI
NaPi
$NaClO_4$
NH_4Pi
NH_4I
KI
KPi
KCNS
$KClO_4$
Me_4NF
Me_4NPi
Me_4NI
$Me_4NFB(C_6H_5)$
Et_4NCl
Et_4NPi
Et_4NI
$n\text{-}Pr_4NI$
$n\text{-}Pr_4NPi$
$n\text{-}Bu_4NCl$
$n\text{-}Bu_4NBr$
$n\text{-}Bu_4NI$
$n\text{-}Bu_4NClO_4$
$n\text{-}Bu_4NNO_3$
$n\text{-}Bu_4NPi$
$n\text{-}Bu_4NFB($
Am_4NBr
$n\text{-}Bu_4N\text{-}p\text{-}$

Me = met

Pi = pic

Table 1. Dissociation Constants of Electrolytes in Acetone Solutions

Compound	Temp (°C)	K_d X 10^4	Ref
LiCl	25	0.033	33
LiBr	25	2.14	32
LiI	25	69.1	33
$LiClO_4$	25	2.0	46
LiPi	25	12.2	37, 40
Li p-toluenesulfonate	25	0.096	33
NaI	25	62.5	34
NaPi	25	14.7	37, 40
$NaClO_4$	25	5.44	46
NH_4Pi	25	11.1	38
NH_4I	25	1.59	46
KI	25	55.7	33
KPi	25	34.3	37
KCNS	25	34.0	39
$KClO_4$	25	1.41	46
Me_4NF	25	8.77	37, 40
Me_4NPi	25	149.3	38, 40
Me_4NI	26.6	34.0	36
$Me_4NFB(C_6H_5)_3$	25	69.3	37
Et_4NCl	25	27.0	40, 41
Et_4NPi	25	222.2	37, 40
Et_4NI	26.6	79.0	36
$n\text{-}Pr_4NI$	26.6	80.0	36
$n\text{-}Pr_4NPi$	25	370.4	40, 41
$n\text{-}Bu_4NCl$	25	23.3	35
$n\text{-}Bu_4NBr$	25	37.9	37, 40
$n\text{-}Bu_4NI$	25	69.9	37, 40
$n\text{-}Bu_4NClO_4$	25	125.0	37, 40
$n\text{-}Bu_4NNO_3$	25	69.9	37, 40
$n\text{-}Bu_4NPi$	25	588.2	37, 40
$n\text{-}Bu_4NFB(C_6H_5)_3$	25	197.0	37
Am_4NBr	25	45.5	38, 40
$n\text{-}Bu_4N$-p-toluenesulfonate	25	24.6	33

Me = methyl Pr = propyl Bu = butyl Am = amyl

Pi = picrate

Table 2. D

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Compound
LiBr
KI

Table 2. Different K_d Values of LiBr and KI from Conductance Measurements

Compound	$K_d \times 10^4$	Investigators	Ref
LiBr	2.14	Nilsson, Wikander and Beronius	32
	2.19	Savedoff	33
	4.49	Dippy, Jenkins and Page	43
	2.56	Pistoia, Polcaro and Schiavo	44
	15.7	Singh and Mishra	45
KI	55.7	Savedoff	33
	91.3	Dippy and Hughes	42
	80.2	Reynolds and Kraus	37
	93.0	Walden, Ulich and Busch	41
	186.0	Dippy, Jenkins and Page	43
	119.3	Hartley and Hughes	42
	297.0	Bauer	42

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that the lithium bromide ion pairs are unreactive species. Assuming contact ion pairs, they calculated the ion pair dissociation constant as 2.33×10^{-4}, in close agreement with the value obtained from conductance measurement.

There are numerous reports in the literature on the influence of metal salts on the vibrational spectrum of acetone (48-58). Most of these studies were carried out in the 4000 to 400 cm^{-1} spectral range and nearly all measurements were made in pure acetone as solvent. The primary emphasis in these studies has been on the changes in the infrared and Raman spectra of acetone upon addition of the salts. The results obtained were interpreted in terms of a complex formation between the cation and the carbonyl group of acetone. The frequency shifts in the acetone bands were found to be independent of anions. The appearance of a band in the 420-430 cm^{-1} region of lithium perchlorate-acetone solutions was observed by Pullin and Pollock (48) and was attributed to a higher frequency component of the 380 cm^{-1} acetone band. Driessen and Groeneveld (56), in their study of solid acetone complexes of alkaline earth and transition metals, also recorded a band at about 420 cm^{-1} which is cation dependent. They assigned this band to the shifting of the 380 cm^{-1} acetone band.

Yamada (50) also studied the effect of lithium and sodium perchlorates on the $n - \pi^*$ transition of acetone in the ultraviolet spectral region, and found that the absorption band for this transition is shifted to shorter wavelength upon addition of the two salts. The effect is more pronounced in the case of the lithium perchlorate. These results are interpreted in terms of a charge transfer complex formation between the alkali metal ion and the acetone molecule. Assuming this type of interaction, the author calculated the percent

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covalent character of the oxygen-lithium and oxygen-sodium bonds to be 13% and 8% respectively.

In their infrared study of silver and lithium perchlorates in acetone solutions, Pullin and Pollock (48) reported that at lithium perchlorate mole fraction of about 0.3, the uncomplexed acetone bands at 1225 cm^{-1} and 530 cm^{-1} disappeared completely and were replaced by the complexed acetone bands at 1239 cm^{-1} and 540 cm^{-1}. They proposed that at high concentration the association of acetone with the metal ion can be expressed by $M^+(acetone)_2$. In less concentrated solutions the number of acetone molecules in the complex may be higher. By measuring the ultrasonic velocity in the lithium perchlorate in acetone solutions, Fogg (59) determined the solvation number of lithium perchlorate as varying from 1.2 to 3.4 in the concentration range studied (0.34 to 0.014 M), and indicated that at infinite dilution the solvation number would be about 4.

Vapor pressure osmometric studies of metal salts in acetone are rather sparse. Peska, et al. (60) determined the apparent molecular weights, M_{app}, of sodium perchlorate and potassium thiocyanate by thermoelectric method. The apparent molecular weights for both salts were found to be strongly concentration dependent. The authors calculated M_{real} from M_{app} by using the osmotic coefficients from vapor pressure osmometric measurement and the degrees of association from conductance measurement. Sokolov and Lindberg (61) studied the effects of concentration and temperature on the M_{app} of sodium iodide in acetone solutions by osmometric measurements. They also calculated the dissociation constants of the salt at various concentrations and temperatures. Both M_{app} and K_d were found to be concentration and temperature dependent.

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Acetic Acid

Popov (62), in his review chapter on anhydrous acetic acid, begins his chapter by stating, "Acetic acid shares with ammonia the distinction of being one of the two most investigated non-aqueous solvents." The statement is amply verified by over 400 references cited in the review chapter.

Acetic acid is a protic solvent with a low dielectric constant of 6.2, and a reasonably wide liquid range (from 16.6° to 117.7°C). It is a highly associated liquid, and because of its poor donor properties, only a limited number of inorganic compounds are soluble in the medium (62).

Many studies on ionic dissociation of inorganic electrolytes in acetic acid solutions have been reported in the literature. Most of them are conductance studies. Some potentiometric and spectrophotometric measurements have also been reported. A detailed discussion on the various studies and the results obtained can be found in Reference (62). The ion pair dissociation constants of alkali metal, ammonium and tetraalkylammonium salts in acetic acid solutions are given in Table 3. Again, as in the case of ion pair dissociation constants of electrolytes in acetone, where several studies have been reported, the agreement is less than desirable.

From Table 3, it is seen that the ion pair dissociation constants for electrolytes in acetic acid is generally smaller by two to three orders of magnitude than those in acetone. Thus it is to be expected that the salts will exist in acetic acid solutions primarily as ion pairs or higher ionic aggregates.

Table 3. D

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Compound
LiCl
LiBr
Li(HCOO)
LiOAc
$LiClO_4$
NaBr
Na(HCOO)
NaOAc
$NaClO_4$
KCl
KBr
K(HCOO)
KOAc
NH_4OAc
RbOAc
CsOAc
Et_4NPi

OAc = acet

Pi = picra

Table 3. Dissociation Constants of Electrolytes in Acetic Acid Solutions

Compound	Temp (°C)	K_d X 10^7	Method	Ref
LiCl	25	0.83	Potentiometric	67
LiBr	30	7.2	Conductance	66
Li(HCOO)	30	0.87	Conductance	66
LiOAc	30	6.0	Conductance	66
$LiClO_4$	25	49	Potentiometric	70
NaBr	30	1.3	Conductance	66
Na(HCOO)	30	0.65	Conductance	66
NaOAc	30	2.1	Conductance	66
$NaClO_4$	25	33	Potentiometric	67
KCl	25	1.3	Potentiometric	67
KBr	30	1.1	Conductance	66
K(HCOO)	30	1.1	Conductance	66
KOAc	30	3.6	Conductance	66
NH_4OAc	25	1.00	Spectroscopic	68
RbOAc	25	1.28	Spectroscopic	68
CsOAc	25	1.66	Spectroscopic	68
Et_4NPi	25	16.3	Conductance	69

OAc = acetate

Pi = picrate

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Numerous spectral studies dealing with the acetate ion as ligand have been reported in the literature. However, relatively very few studies have been done on inorganic complexes containing acetic acid molecules as ligands. A detailed review on the subject can be found in Reference (62). Recently Groeneveld, et al. (63) reported the preparation of some complexes of the divalent cations magnesium, manganese, cobalt, nickel, copper and zinc with acetic acid as ligands. The compounds were prepared from the hydrated salts (with tetrafluoroborate, perchlorate and nitrate anions) and acetic anhydride. The metal ions are coordinated to six acetic acid molecules forming hexacoordinated complex cations. Spectral studies showed that the acetic acid molecules are bound to the metal ion via the carbonyl oxygen. Earlier studies (62) of other complexes also indicate that the carbonyl oxygen is the coordinating site.

Cryoscopic studies (64,65) showed that lithium salts are polymerized in acetic acid solutions. Isolations of some addition compounds of alkali metal salts with acetic acid have also been reported (62). The compounds have either 1:1 or 1:2 stoichiometry, e.g., LiOAc·HOAc, KOAc·HOAc, LiCl·2HOAc and LiI·2HOAc.

Tetrahydrofuran

Tetrahydrofuran is a solvent with moderate liquid range (-65° to 66°C). It is relatively non-polar, with a dielectric constant of 7.39 at 25° (71). The donor number of the solvent is 20 (29), slightly higher than that of acetone.

Several spectroscopic solvation studies in tetrahydrofuran solutions have been reported in recent years (9,10,12,13,26,27,72,76).

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In contrast to the alkali ion solvation bands observed in dimethyl sulfoxide (1) and pyrrolidones (2), the alkali ion vibrations in tetrahydrofuran solutions are strongly anion dependent, indicating presence of ion pairs or higher ionic aggregates. The reported frequencies are tabulated in Table 4.

Day and co-workers studied the complexation between sodium tetrabutylaluminate ($NaAlBu_4$) and tetrahydrofuran in cyclohexane solutions. In their more ratio studies, using both proton magnetic resonance (27) and infrared (76) techniques, they showed the formation of 1:1 and 1:4 complexes, depending on the respective concentrations of the two interacting species. The over-all equilibrium expression is:

$$Na\cdot THF^+, AlBu_4^- + 3\ THF \rightleftarrows Na\cdot 4THF^+, AlBu_4^-$$

There are only a few reports in the literature (71-75) on conductance studies in tetrahydrofuran solutions. Szwarc, <u>et al</u>. (71,74) determined the conductances and the dissociation constants of a series of tetraphenylborates in tetrahydrofuran solutions. From the data obtained, they concluded that the lithium and sodium salts are the most dissociated, while the cesium and tetraalkylammonium salts, in spite of their bulkiness, are less dissociated than the sodium or lithium salts, indicating weaker or lack of solvation of the bulkier cations. The ion pair dissociation constants obtained by Szwarc, <u>et al</u>., together with that of lithium chloride (75), are listed in Table 5.

Edgell, <u>et al</u>. (72) measured the conductances of tetrahydrofuran solutions of sodium tetracarbonylcobaltate ($NaCo(CO)_4$) at various concentrations. In the equivalent conductance <u>vs</u>. square root of

Table 4.

Compound
LiCl
LiBr
LiI
$LiNO_3$
$LiBPh_4$
LiCo(CO)
NaI
$NaBPh_4$
NaCo(CO)
$NaAlBu_4$
$KAlBu_4$
KCo(CO)

Table 4. **Frequencies of Alkali Ion Vibrations in Tetrahydrofuran Solutions**

Compound	$\nu(cm^{-1})$	Ref
LiCl	387	10
LiBr	378	10
LiI	373	10
$LiNO_3$	407	10
$LiBPh_4$	412	10
$LiCo(CO)_4$	413	10
NaI	184	10
$NaBPh_4$	198	10
$NaCo(CO)_4$	192	10
$NaAlBu_4$	195	13
$KAlBu_4$	150	13
$KCo(CO)_4$	142	10

Table 5. Di

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Compoun
LiCl
LiBPh$_4$
NaBPh$_4$
KBPh$_4$
CsBPh$_4$
Bu$_4$NPh$_4$
Bu(isoamy

Ph = phen

Bu = buty

Table 5. Dissociation Constants of Electrolytes in Tetrahydrofuran Solutions

Compound	Temp (°C)	K_d X 10^5	Ref
LiCl	20	0.000012	75
$LiBPh_4$	25	7.96	74
$NaBPh_4$	25	8.52	74
$KBPh_4$	25	3.22	74
$CsBPh_4$	25	0.187	74
Bu_4NPh_4	25	4.32	74
$Bu(isoamyl)_3NPh_4$	25	6.04	74

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Bu = butyl

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concentration plot, a deep minimum was evident at low concentration ($\sqrt{C} \approx 0.1$ M) and there was an inflection point at higher concentration ($\sqrt{C} \approx 0.3$ M). They postulated the formation of ion pairs in dilute tetrahydrofuran solutions, and the formation of ionic clusters, e.g., triplets and quadruplets, in the more concentrated solutions.

Dimethyl Sulfoxide

Dimethyl sulfoxide has a relatively high dielectric constant of 46.6 (77), and a broad liquid range of 18.4-189°C (78). It is a good donor solvent, with a donor number of 30 (29). A detailed discussion of solvation studies in dimethyl sulfoxide can be found in Reference (1). In dimethyl sulfoxide, the frequencies of the far infrared solvation bands are independent of anions. Bands due to the cations lithium, ammonium, sodium, potassium, rubidium, and cesium occur at 430 cm^{-1}, 214 cm^{-1}, 200 cm^{-1}, 154 cm^{-1}, 125 cm^{-1}, and 110 cm^{-1}, respectively. The solvation numbers, as determined by proton magnetic resonance mole ratio studies, are 2 for lithium ion (1) and 6 for sodium ion (2).

Conductance studies (79-85) in dimethyl sulfoxide solutions reported in the literature indicate that, in dilute solutions, with few exceptions, electrolytes are generally completely dissociated.

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III. EXPERIMENTAL SECTION

Reagents

Acetone: Matheson Coleman & Bell reagent grade acetone was stored over calcium sulfate several days and then fractionally distilled from fresh calcium sulfate through a one meter packed column. The middle fraction boiling at 54°C at 737 mm (lit. (31): 56.1°/760 mm) was collected. The water content was approximately 0.02%.

Acetone-d_6: Diaprep Inc., acetone-d_6 with a minimum isotopic purity of 99.5% was used without further treatment.

Acetic Acid: Fisher reagent grade 99.7% acetic acid was purified by addition of approximately 1% (by volume) of acetic anhydride, the mixture was refluxed for several hours and then fractionally distilled through a one meter packed column. The purified acetic acid melted at 16.6 $\pm$ 0.2°C (lit. (62): m.p. = 16.635°C). The water content was approximately 0.01%.

Acetic Acid-d_4: Diaprep Inc., acetic acid-d_4 with a minimum isotopic purity of 99.5% was used without further purification.

Dimethyl Sulfoxide: Baker reagent grade dimethyl sulfoxide was purified by refluxing under high vacuum (4 mm or less) for several hours over barium oxide, and then fractionally distilled through a 30 cm packed column. Throughout the vacuum distillation, the temperature was maintained at approximately 45°C. The middle fraction

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fraction was collected and subjected to fractional crystallization three times. The purified product melted at 18.3 ± 0.2°C. The best literature value of 18.45° (78) can be achieved only after very elaborate and tedious purification procedures. The water content was approximately 0.01%.

Nitromethane: Matheson, Coleman and Bell practical grade nitromethane was purified by percolation through a 20-cm column of Dowex 50W-X8 cation-exchange resin (86). The eluent was refluxed over anhydrous calcium sulfate for several hours and then fractionally distilled through a one meter packed column. The middle fraction boiling at 99.5°C at 738 mm was collected (lit. (87): $b.p._{760} = 101.25°$). The water content was approximately 0.1%.

Tetrahydrofuran: Matheson, Coleman and Bell reagent grade tetrahydrofuran, with water content of approximately 0.02%, was used without further purification.

Tetrahydrofuran-d_8: Norell Chemical Company, Inc., tetrahydrofuran-d_8 with a minimum isotopic purity of 99% was used without further treatment.

Lithium Thiocyanate: Lithium thiocyanate from City Chemical Corporation, N.Y., could not be dried by simple heating. The salt dissolved in its water of hydration when the temperature was raised to about 40°C. Anhydrous lithium thiocyanate was prepared (88) by first dissolving the salt in anhydrous ether, then adding about 2 volumes of petroleum ether. If sufficient water were present in the compound, two immiscible liquid phases would form. The aqueous phase at the bottom was removed by decantation. An etherate precipitate, $LiSCN\cdot(C_2H_5)_2O$, crystallized upon cooling and stirring. The etherate crystals were filtered with minimum exposure to moist air. The ether

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air. The ether in the etherate was removed under high vacuum at 30°C (~1 day). Then the temperature in the vacuum oven was raised gradually. Lithium thiocyanate was finally dried over phosphorus pentoxide under vacuum at 90°C for 2 days. The dried product has a melting point range of 279-282°C (Lit. (88): m.p. = 281°), and a water content of 0.4%.

Lithium Iodide: Anhydrous lithium iodide from K & K Laboratories was found to contain over 3% water. Heating the salt in vacuum resulted in hydrolysis and decomposition (89). However, the water content can be reduced by recrystallization from acetone (90). The salt was dissolved in purified acetone and precipitated as the acetonate by cooling the solution in a dry ice bath. The acetonate crystals were filtered with minimum exposure to air. The procedure was then repeated. The acetonate crystals were then heated over phosphorus pentoxide under vacuum at 35°C for 1 day. The temperature was then raised gradually until final drying at 85°C for 3 days. Lithium iodide thus obtained had a water content of 0.6%.

Lithium Tetraphenylborate: Lithium tetraphenylborate was prepared by metathesis of excess lithium chloride and sodium tetraphenylborate in tetrahydrofuran solution (74). Lithium chloride and sodium tetraphenylborate in the mole ratio of approximately 2:1 were dissolved separately in tetrahydrofuran. After mixing the solutions, the less soluble sodium chloride was filtered out, and the tetrahydrofuran evaporated off by blowing a stream of nitrogen over the solution. The residue was dissolved in 1,2-dichloroethane and the solution was filtered to remove excess lithium chloride. Lithium tetraphenylborate was then precipitated by the addition of cyclohexane. After filtration, the procedure was repeated twice. The salt was dried wer pho

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over phosphorus pentoxide under vacuum at 60°C for 3 days. Flame emission analysis showed the sodium content was about 0.05% and the lithium content 2.0 ± 0.2% (theoretical: 2.15%). The water content was approximately 0.4%.

Other Alkali Metal Salts: All other alkali metal salts, with the exceptions of sodium thiocyanate, sodium tetraphenylborate, ammonium thiocyanate, potassium thiocyanate, were reagent grade chemicals and were used after drying at 180-200°C for 2-3 days. Sodium thiocyanate, sodium tetraphenylborate, ammonium thiocyanate and potassium thiocyanate were vacuum dried at 60°C for 3 days prior to use. The preparation of ^{6}Li salts has been described previously (91).

Tetraalkylammonium Salts: Tetra-n-propylammonium bromide, tetra-n-butylammonium bromide, tetra-n-butylammonium iodide from Eastman Kodak, tetramethylammonium fluoride from Aldrich Chemical Co. Inc., and tetra-n-butylammonium perchlorate from K & K Laboratories, all were vacuum dried at 60°C for 3 days prior to use.

Benzil : Eastman Kodak reagent grade benzil was recrystallized twice from absolute ethanol and then vacuum dried at 50°C for 2 days. The purified product melted at 96 ± 0.5°C (92).

Biphenyl: Eastman Kodak reagent grade biphenyl was used without further treatment.

Analyses

All quantitative determinations of water were carried out by the Karl Fischer procedure (93).

Flame emission analyses of sodium and lithium were performed by using a Beckman Model B Spectrophotometer with flame photometry attachment.

The isotopic purity of all deuterated solvents was checked by mass spectrometry, a service provided by this Laboratory.

Preparation of Salt Solutions

All the salt solutions were prepared on a molar basis.

In mole ratio and mixed solvents studies, several stock solutions of various concentrations of one solvent in another were first prepared, and solutions of intermediate or lower concentrations were made by dilution.

In vapor pressure osmometry studies, salt solutions of the highest concentrations were first prepared, and subsequent series of solutions were prepared by dilution.

Since most of the solvents and salts employed in these studies were hygroscopic, care was taken to prepare them in as nearly an anhydrous condition as possible. During preparation or transfer, exposure of the solvents and solutions to the air was minimized by making all transfers with a syringe or pipet. Measurements were made immediately after preparation of solutions. Solutions were prepared at room temperature of about 24°C.

Instrumental Measurements

Far Infrared Measurements: Most of the far infrared spectra (from 600-80 cm^{-1}) were obtained with the Perkin Elmer 301 Far Infrared Spectrometer. Some spectra were obtained with the Digilab FTS-16 Interferometer. The Perkin Elmer 301 instrument was operated in the double beam mode, and single beam mode was used in the operation of the Digilab FTS-16 Interferometer. Nitrogen was used to purge the instruments of water vapor prior and throughout the measuremen

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measurements. Polyethylene cells with 0.1 or 0.2 mm pathlengths, purchased from Barnes Engineering Co., were used.

The frequency scale of the Perkin Elmer 301 Spectrometer was calibrated with water vapor. Detailed calibration procedure has been previously described (2).

In cases where duplicate measurements were made from the two instruments, the solvation band frequencies always agreed to ±3 cm^{-1}, which is within experimental uncertainty.

Infrared Measurements: All infrared spectra in the 4000-600 cm^{-1} region were obtained on a Perkin Elmer Model 225 Spectrometer. Nitrogen was used to purge the instrument of water vapor throughout the measurements. Standard demountable liquid cells, with KBr windows and teflon spacers giving pathlengths from 0.025 to 0.1 mm, all obtained from Barnes Engineering Co., were used. Filling of the liquid cells was done by using small volume syringes to insure uniformity and minimize sample exposure to the atmosphere.

Raman Measurements: Raman spectra were obtained using a Spectra-Physics Model 700 Raman Spectrometer, with a 40 mW 6328 Å He-Ne laser. The frequency scale was calibrated with carbon tetrachloride Raman lines.

Nuclear Magnetic Resonance Measurements: Varian Associates A56/60D Spectrometer was used to obtain all nuclear magnetic resonance spectra. Tetramethylsilane was used as an internal standard for all samples.

Vapor Pressure Osmometric Measurements: Vapor pressure osmometry studies were performed using a Mechrolab Inc., High Temperature Vapor Pressure Osmometer Model 302. The method outlined in the operational

manual was used (94). The sample chamber was maintained at a constant temperature of 37°C, and at least 4 hours were allowed for it to equilibrate and saturate with solvent vapor prior to measurements. Benzil was used as calibration standard for all the solvents. The concentrations ranged from 0.02 to 0.2 M for benzil, and 0.02 to 0.16 for other salts. Biphenyl was used as an additional check on the calibration constants obtained from benzil.

In all the measurements, the solvent and sample drops at the thermister beads were kept at approximately the same size. The resistance ΔR values were recorded 2 minutes (accurate to within 5 seconds) after the sample drops were deposited to the thermister bead. Approximately 15-20 minutes prewarm periods were allowed for each solution. The solvent in the solvent cup (used to saturate the chamber) was replaced after every two or three series of runs. At least two readings of ΔR were taken for each solution and the averaged value was used for calculations.

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IV. THERMOELECTRIC VAPOR PRESSURE OSMOMETRY

Thermometric vapor pressure osmometry was first introduced by Hill (95). The determination of the molecular weight of a substance by the method of vapor pressure osmometry involves the following steps. An enclosed chamber is thermostated and saturated with solvent vapor. A drop of the solution of the substance studied is placed on one of the two matched thermistor beads and a drop of solvent on the other. Since the vapor pressure of the solution drop is lower than that of the solvent, solvent vapor will condense on it, the heat of condensation will raise its temperature, and a steady state is soon reached. The steady state temperature difference between the two drops is proportional to the vapor pressure difference. The change in resistance, ΔR, generated by the temperature difference ΔT, is measured by a Wheatstone bridge. The value ΔR is used to calculate the molecular weight of the unknown substance by methods described below.

When this technique was first introduced, thermopiles were used to measure the temperature difference, and the method was used exclusively for aqueous systems. Subsequently, the speed and the sensitivity of the measurements were greatly improved by using thermistors, and the method was adapted to organic solvents (96-100). The theory and the limitations of the method has been discussed by several authors (92,100-106). Presently, matched thermistors are almost exclusively used for measuring the temperature difference, and besides the determination of molecular weights, an increasing use of vapor pressure osmometry for the determination of osmotic and activity coefficients of salts in nonaqueous solvents has been reported (101,107-111). There are also several reports on the use of vapor pressure osmometry for the study of association or aggregations of salts in nonaqueous solvents (112-115).

In this study, the Mechrolab Vapor Pressure Osmometer Model 302 was used (see Chapter II). It is stated in the Mechrolab Instruction Manual (94) that the sample and solvent drop size variations have no appreciable effect on the value of molecular weight determined, except in the case of solvents with high surface tensions. The statement has been disputed by Meeks and Goldfarb (116), who studied the quantitative effects of the drop size and the time variations on the value of the measured molecular weight. They found that the vapor pressure osmometer readings ΔR (and hence, the molecular weight) are strongly dependent on drop size and time variations, and proposed methods for correcting both of these effects.

The molecular weights as determined by vapor pressure osmometry are the so-called number-average molecular weight. The term "number-average" indicates that every molecule present, regardless of its size and mass, gives rise to the same response. In order for this to be achieved, the system must behave ideally, i.e., the force of interaction (solute-solute, solute-solvent, solvent-solvent) should be the same for all molecules present in solution. In general, near ideal conditions are reached in the limit at infinite dilution and the response will be proportional to the number of molecules present.

However, departures from the ideal behavior of the systems can still result from association or dissociation of the solute or solvent.

There are two steps involved in the determination of molecular weight of the substance studied: (i) calibration of the instrument, and (ii) measurement of the unknown. For each solvent, a calibration constant K for the instrument used has to be found. The calibration constant is determined by use of a standard substance of known molecular weight which gives near ideal solution at low concentrations.

Several methods have been proposed for the determination of the calibration constant and the molecular weights. Only the two methods used in this study will be discussed.

(I) The limiting slope method (117) (or "constant K" method by the Mechrolab Manual): For small temperature changes observed in this work, the results can be represented by the equation

$$\Delta R = a_0 + a_1C + a_2C^2 + a_3C^3 \ . \ . \ . \qquad (1)$$

where ΔR is the osmometer dekastat reading observed at a solution concentration C. The coefficient a_0 represents the zero point displacement and normally should be zero. The coefficient a_1 can be expressed as K/M_n where K is the calibration constant and M_n is the number-average molecular weight. Thus this is the coefficient of interest. The term a_3C^3 is normally small enough to be negligible. The term a_2C^2 is usually large and cannot be neglected. However, the coefficient a_2 is not required for calculating apparatus constants or molecular weights. It is required to evaluate the data and in error considerations (117). Hence for general cases,

equation (1) is reduced to

$$\Delta R = a_1 C + a_2 C^2 \; . \; . \qquad (2)$$

Equation (2) can be rewritten as

$$\Delta R/C = a_1 + a_2 C \; . \; . \qquad (3)$$

Therefore, a plot of $\Delta R/C$ vs. C should give a straight line with intercept a_1 and slope a_2. In cases where scattering or nonlinearity of points at low concentrations are encountered, the higher concentration points are emphasized. Thus

$$(\Delta R/C)_{C=0} = a_1 = K/M_n$$

If molar concentration is used for the calibration plot, then $(\Delta R/C)_{C=0} = K_m$ in units of ohms liters/mole.

For a molecular weight determination, similar $\Delta R/C$ vs. C plots are obtained. However, C is expressed in g/liter, so that the molecular weight is calculated from the expression,

$$M_n = K_m \div (\Delta R/C)_{C=0} \quad \text{(C in unit g/l)}$$

(II) The "variable K" method: In this method, the calibration graph is obtained by plotting $\Delta R/C_m$ vs. ΔR. The ΔR value of each concentration of sample is entered into the calibration plot to find $\Delta R/C_m$, from which a series of apparent C_m values can be calculated. The reciprocal apparent molecular weight of each solution is obtained by dividing each C_m value by weight concentration of the solution. A plot of the reciprocal of apparent molecular weight ($1/M_{app}$) vs. weight concentration is extrapolated to zero concentration to obtain the $1/M_{app}$ value at zero concentration. Reciprocal of $(1/M_{app})_{C=0}$ is the number-average molecular weight.

In the present study, no attempt is made to extrapolate to zero concentration and find the number-average molecular weight by method (II). Instead the apparent molecular weight for each concentration is calculated and then plotted vs. the actual concentration (from weight of solute used in preparing the solution) so as to elucidate the magnitude of the concentration dependence of the apparent molecular weight of each electrolyte.

V. RESULTS AND DISCUSSION

(A) Acetone

Far Infrared and Raman Spectra

Preliminary investigations in the 600-80 cm^{-1} infrared region indicated that some spectral windows are available in acetone. The solvent has strong fundamental bands at 528 cm^{-1}, 390 cm^{-1}, and a weak band at 495 cm^{-1}. It has a narrow spectral window between 480 and 410 cm^{-1}, and is fairly transparent in the 360 to 150 cm^{-1} spectral region.

Solutions of common lithium and sodium salts were studied in the far infrared region and new, broad absorption bands were observed. The new bands could not be ascribed to the solvent or to the anions of the salts. The exact positions of the band maxima were obtained by subtracting out the solvent absorption. The frequencies of the new bands are cation dependent, e.g., 425 cm^{-1} for lithium perchlorate and 195 cm^{-1} for sodium perchlorate in acetone solutions. Thus the new bands were assigned to the cation (or salt) - acetone vibrations. A summary of the data obtained is given in Table 6.

It is seen from the data that for lithium salts with polyatomic anions as well as for the iodide, the band frequencies do not depend on the mass or the nature of the anion. There is, however, a decrease in the frequency of the observed band for the bromide (412 cm^{-1}) and the chloride (409 cm^{-1}), with the chloride having the lowest band frequency. Anion dependence of the bands was also observed in spectra

Table 6. Absorption Bands (cm^{-1}) of Alkali Metal Salts in Acetones

Salt	Acetone	Acetone-d_6
$LiClO_4$	425 ± 3	390 ± 4
LiSCN	425	390
$LiBPh_4$	426	390
$LiNO_3$	420	387
LiCl	409	376
LiBr	412	378
LiI	423	389
NH_4SCN	212 ± 4	
NaSCN	196	192 ± 5
$NaClO_4$	195	191
$NaBPh_4$	196	190
NaI	192	186
KSCN	154	
$^6LiClO_4$	436 ± 3	
$^6LiNO_3$	434	
^6LiCl	412	
^6LiBr	420	
^6LiI	436	

of lithium salts in acetone-d_6 solutions, where lithium salts with polyatomic anions, as well as the iodide, show bands at about 390 cm^{-1}, while the bromide and chloride salts give bands at 378 cm^{-1} and 376 cm^{-1}, respectively. The large shift of about 35 cm^{-1} with deuterated solvent is unexpected since a Hook's law calculation, based on a pseudo-diatomic situation in which the acetone and acetone-d_6 molecules are considered as point masses in the same manner as the lithium atoms, predicts a shift of only two cm^{-1}. A similar Hook's law calculation of the effect of substitution of ^6Li salts in place of the naturally occuring ^7Li salts predicts a shift of 30 cm^{-1}. Experimentally the shift is found to be approximately 10 cm^{-1} except in the case of the lithium chloride salts where the shift is only 3 cm^{-1}. No valid explanation can be given for this discrepancy at this time. It seems reasonable to assume that the vibrating species is complex, involving the cation, the solvent molecules and in some cases (especially the bromide and chloride) the anions.

The anion dependence of the lithium bromide and chloride band frequencies is similar to that reported by Edgell, et al. (10), for lithium salts in tetrahydrofuran solutions. However, since the anion dependence of the solvation band does not follow the mass dependence which would be expected if an ion pair vibration (such as was observed by Evans and Lo (11) for some tetraalkylammonium salts in benzene) was being detected, it is quite possible that the anion is acting as a perturbing influence on the cation-solvent vibration. The very small shift (about 3 cm^{-1}) observed for lithium chloride with isotopic substitution of ^6Li may indicate the existence of a contact ion pair - solvent vibration.

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A shoulder at about 365 cm^{-1} was also observed for all the lithium salts in acetone solutions. The shoulder, as will be shown below, is a band which is anion dependent in some cases. It is also dependent on the mass of the cation.

In general at least 0.1 M solutions are required to yield observable spectra. Among the common potassium and ammonium salts only the thiocyanates were found to be sufficiently soluble. A band at 154 ± 4 cm^{-1} was observed for potassium thiocyanate in acetone solution. Ammonium thiocyanate gave a band at 212 ± 4 cm^{-1} and a weak band at about 350 cm^{-1}. The band at 212 cm^{-1} has the shape of the usual solvent-cation vibrational band. The origin of the weak band at about 350 cm^{-1} is uncertain. The solubilities of the more common rubidium and cesium salts (MCl, MBr, MI, MNO_3, $MClO_4$, MSCN, $MBPh_4$) in acetone were too low (less than 0.1 M) to allow meaningful infrared spectral measurements.

A concentration range of between 0.1 and 1.5 M was used to study the lithium and sodium salts. The intensities of the observed cation-solvent bands were proportional to the concentrations in this range. High absorption and high baseline at concentrations higher than about 1.5 M limited further comparison.

The intensity of the 425 cm^{-1} band was also measured as a function of lithium perchlorate concentration in nitromethane solutions which were 1.5 M in acetone. The absorbance at peak maximum of 425 cm^{-1} band was plotted _vs_. molar concentration of lithium perchlorate (Figure 1). A straight line was obtained for solutions which were $\leq$ 0.4 M lithium perchlorate. At higher concentrations, while the plot was still linear, the slope was considerably different. At the same time, while the frequency of the band is not changed

Figure 1. Absorbance of 425 cm^{-1} band *vs*. concentration of $LiClO_4$. Concentration of acetone = 1.5 M. Solvent: nitromethane. A. Without subtraction of baseline. B. With the baseline subtracted.

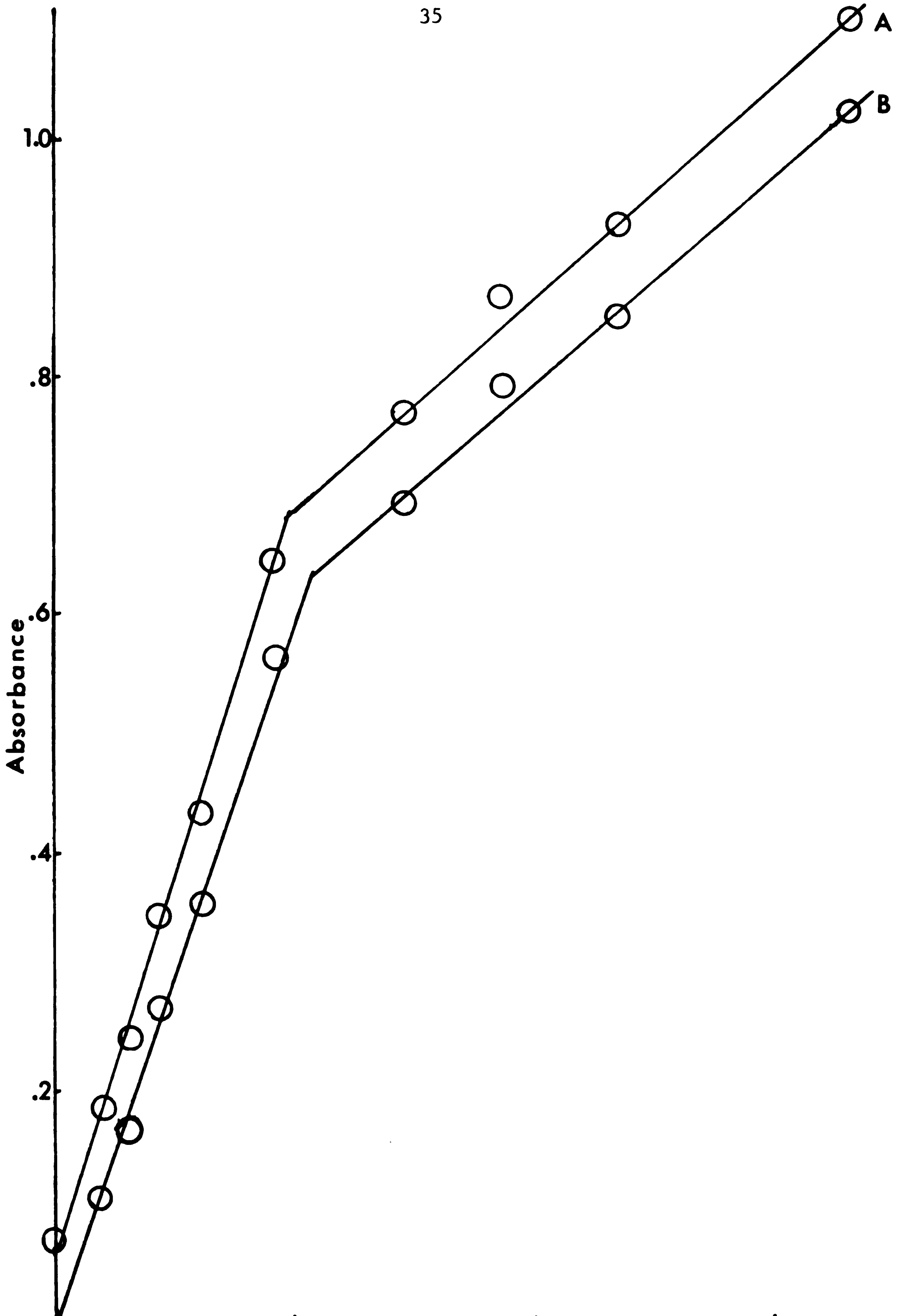

Figure 1.

appreciably, the band begins to broaden. The broadening may indicate that a new absorption band is formed whose frequency does not differ appreciably from that of the original band. The data, therefore, indicate that below 4:1 mole ratio of acetone/Li^+, a new absorbing species is formed. The change in absorbance and the band broadening may be due to a change in the solvation number of the lithium ion or to a replacement of either one or more acetone molecules in the solvation shell by the perchlorate ion (see below).

Raman spectra in the 3000-150 cm^{-1} spectral region were obtained of the lithium nitrate, bromide, and perchlorate and of sodium perchlorate solutions in acetone and in acetone-nitromethane mixtures in the 0.6-3.0 M concentration range. the 425 cm^{-1} Li^+-acetone and 195 cm^{-1} Na^+-acetone bands were not observed. It seems that the bands are Raman-inactive and, therefore, the cation-solvent bonding is essentially electrostatic as postulated by Edgell. et al. (9,10).

Studies of Acetone Vibrations

There are many reports in the literature discussing the influence of metal salts on the vibrational spectrum of acetone (48-58). These studies were carried out in the 4000-400 cm^{-1} range and all measurements were made in pure acetone as solvent. The shifting or splitting of acetone fundamental bands were ascribed to interaction or complex formation between the cation and the carbonyl oxygen of the solvent molecule. However, in pure acetone, the fundamental vibration bands are rather intense, and the observation of the shifting or splitting of those bands relative to salt concentrations is difficult, if not impossible.

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In this study the behavior of the acetone vibrations as a function of acetone/Li^+ mole ratio was observed. It was necessary, therefore, to use an inert solvent as diluent. The difficulties of selecting inert solvents for such studies have been discussed by Wuepper (2). In the present case it was found possible to use nitromethane as the diluent. While it cannot be stated that nitromethane is devoid of all solvating ability, its relative inertness is well known (29) and it is quite unlikely that it can compete significantly with acetone in the solvation of lithium ions.

A series of nitromethane solutions was prepared which were 1.5 M in acetone and contained varying amounts of lithium perchlorate. The changes in the frequencies of four strong acetone vibrational bands at 390, 528, 1224, and 1712 cm^{-1} were followed as a function of acetone/$LiClO_4$ mole ratio.

The 390 (C-C-C deformation), 528 (C-C-O bending) and 1224 cm^{-1} (C-C asymmetric stretch) bands were split, with new bands appearing at 369, 539 and 1239 cm^{-1}. These new bands can be attributed to vibrations of the complexed acetone. The relative intensities of the various bands as a function of acetone/$LiClO_4$ mole ratios are shown in Figures 2,3, and 4. No splitting was observed for the 1712 cm^{-1} C=O stretch, but the band was shifted progressively to lower wave number with decreasing acetone/$LiClO_4$ mole ratio, as shown in Figure 5.

Similar shifting and splitting of the acetone fundamental frequencies were observed with lithium iodide, indicating that the lithium ion is the species that interacts with acetone.

The intensity of the 390 cm^{-1} acetone band decreases gradually with decreasing acetone/$LiClO_4$ mole ratio, and a new band at

Figure 2. Spectra of solutions of acetone + $LiClO_4$ in nitromethane. The 425 cm^{-1} and 390 cm^{-1} bands.

A. Blank = 1.5 M acetone

B. Acetone/$LiClO_4$ ratio = 8:1

C. Acetone/$LiClO_4$ ratio = 4:1

D. Acetone/$LiClO_4$ ratio = 2:1

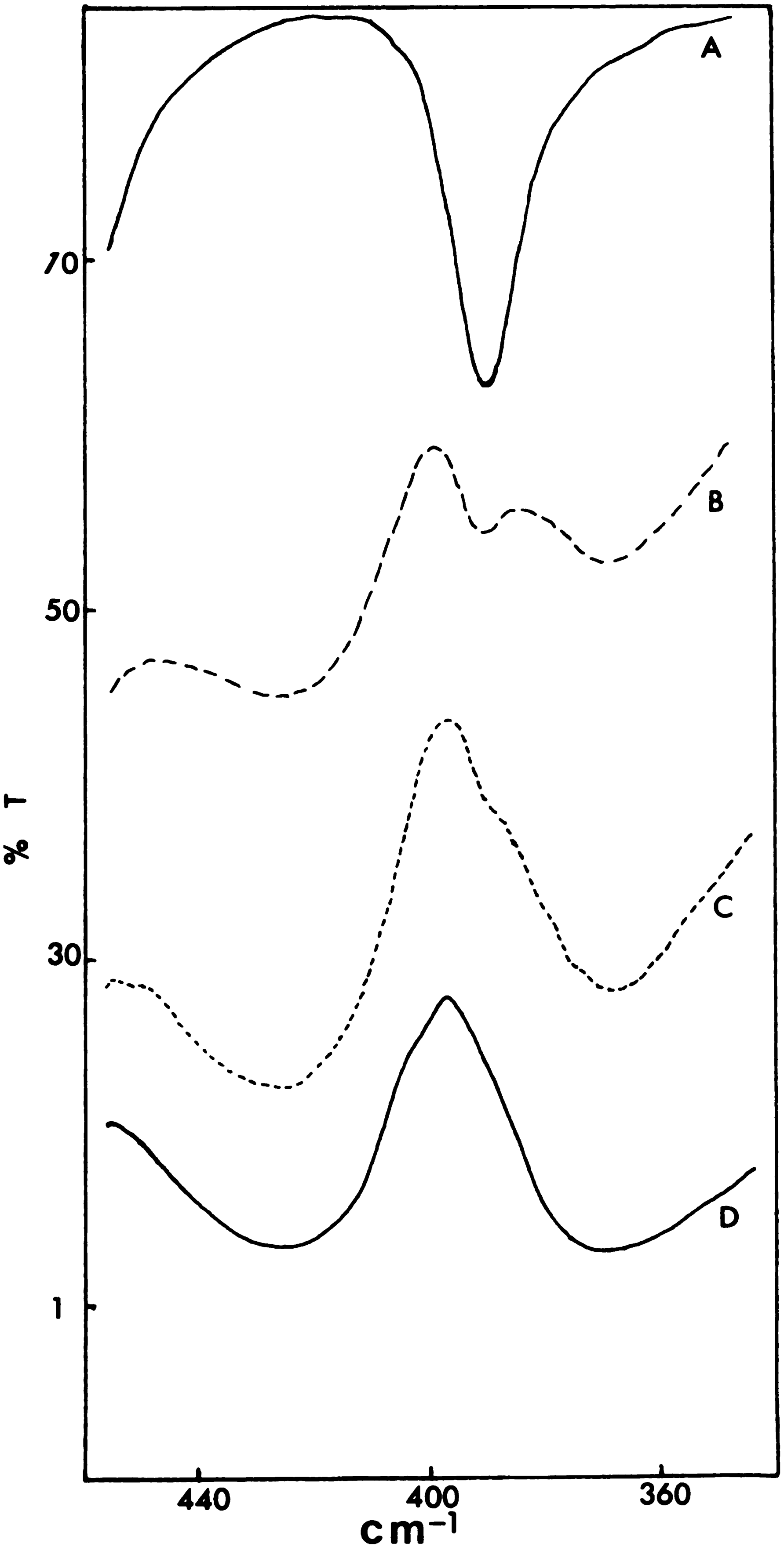

Figure 2.

Figure 3. Spectra of solutions of acetone + $LiClO_4$ in nitromethane. The 528 cm^{-1} band.

A. Blank = 1.5 M acetone

B. Acetone/$LiClO_4$ ratio = 8:1

C. Acetone/$LiClO_4$ ratio = 4:1

D. Acetone/$LiClO_4$ ratio = 2:1

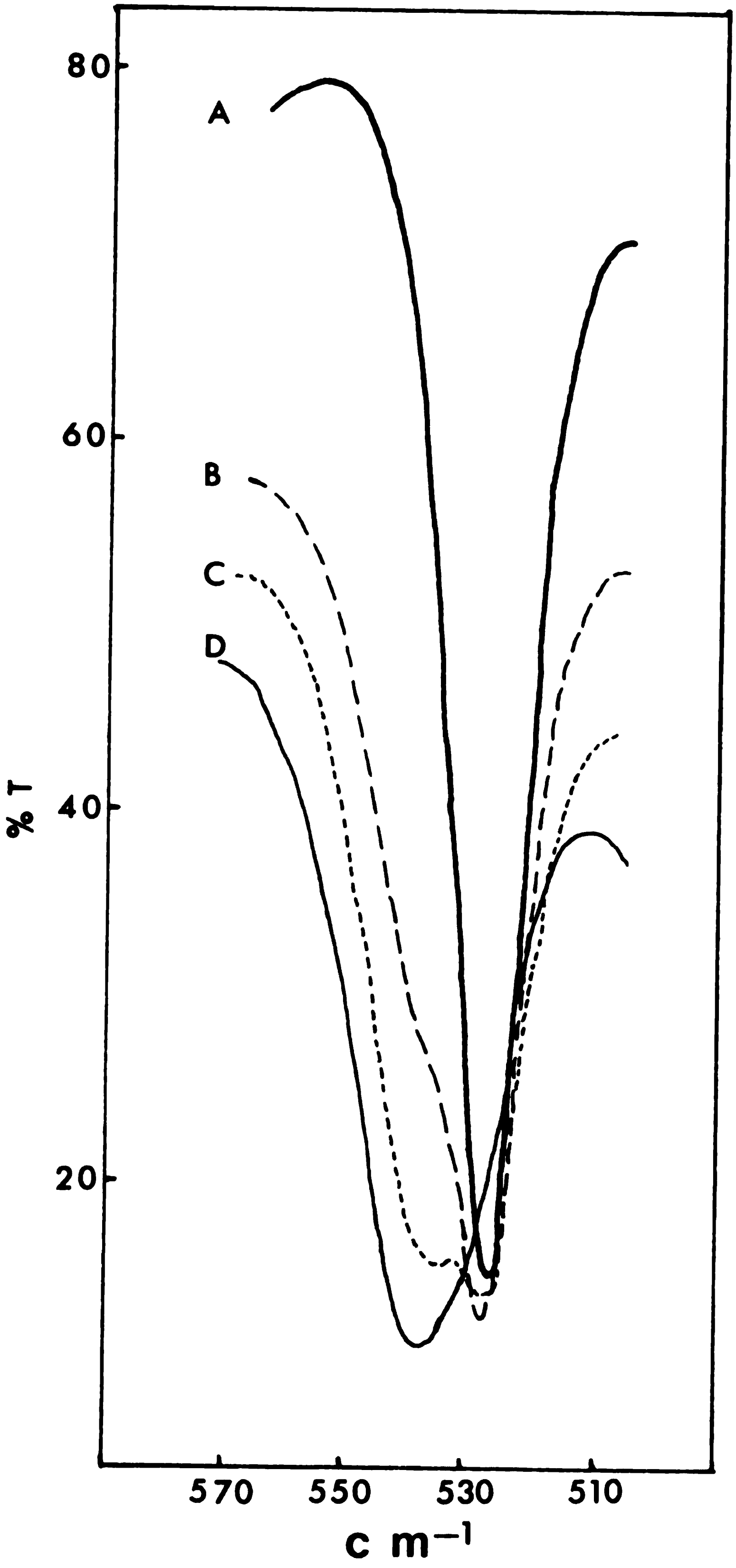

Figure 3.

Figure 4. Spectra of solutions of acetone + $LiClO_4$ in nitromethane. The 1224 cm^{-1} acetone band.

A. Blank = 1.5 M acetone

B. Acetone/$LiClO_4$ ratio = 10:1

C. Acetone/$LiClO_4$ ratio = 4:1

D. Acetone/$LiClO_4$ ratio = 1.7:1

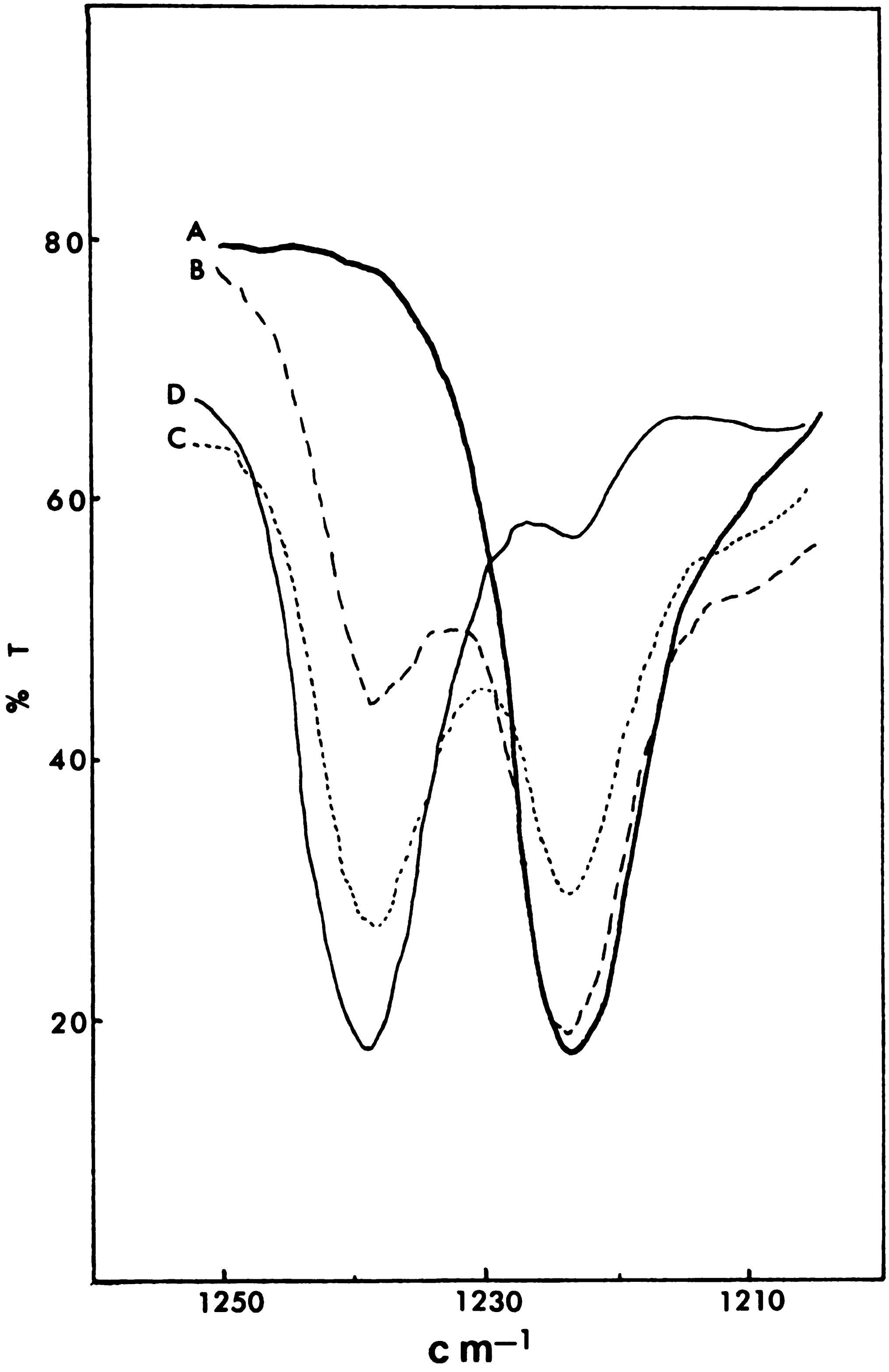

Figure 4.

Figure 5. Spectra of solutions of acetone + $LiClO_4$ in nitromethane. The 1712 cm^{-1} acetone band.

A. Blank = 1.5 M acetone

B. Acetone/$LiClO_4$ ratio = 10:1

C. Acetone/$LiClO_4$ ratio = 4:1

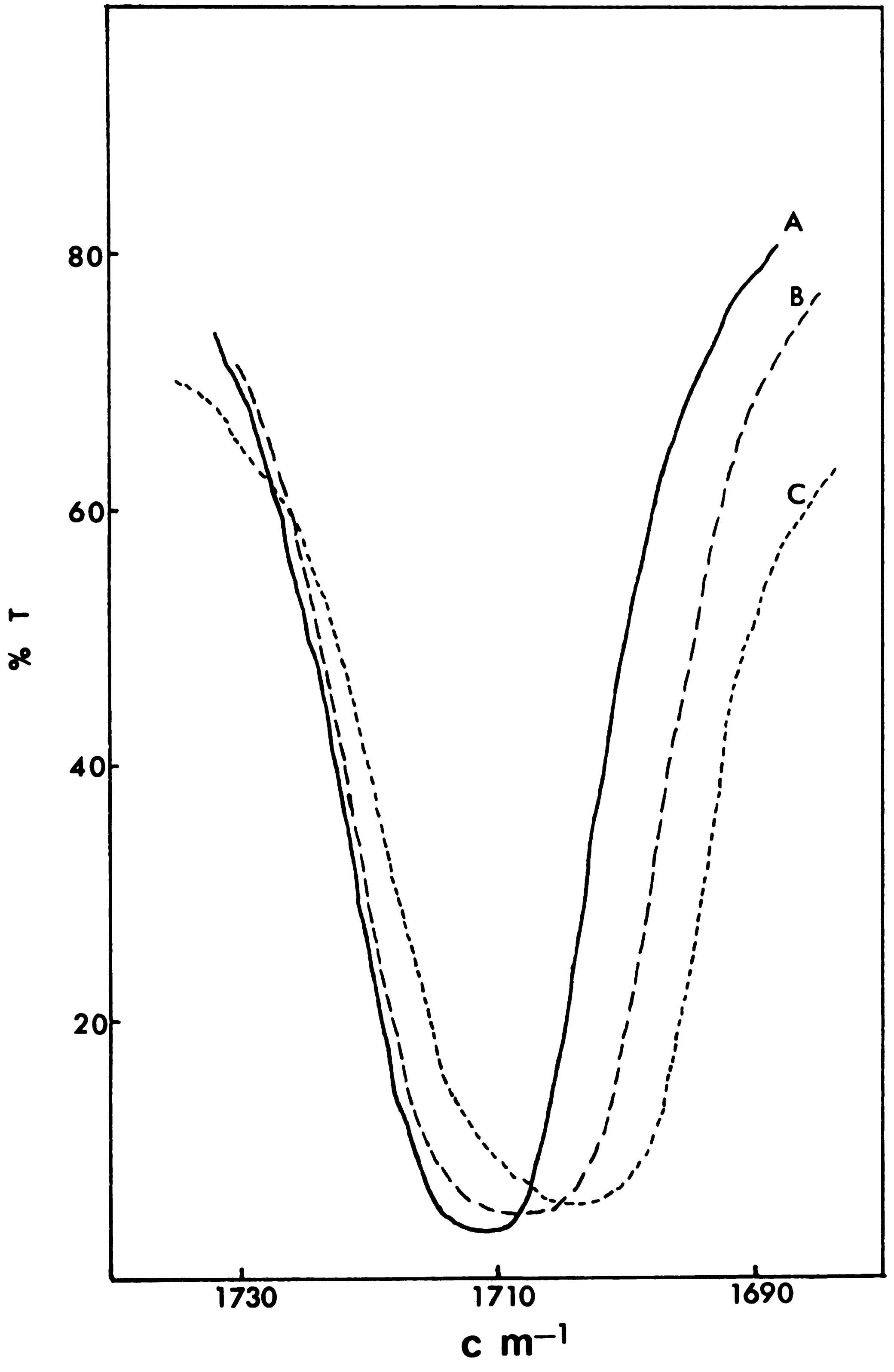

Figure 5.

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Figure 6.

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369 ± 3 cm^{-1} appears. This new band, in contrast to the 1239 and 539 cm^{-1} complexed acetone bands, was observed to be dependent on the mass of the cation. When $^{6}LiClO_4$ was substituted for $^{7}LiClO_4$, the splittings and shiftings of the 1224, 528 and 1712 cm^{-1} acetone bands were identical with those observed with $^{7}LiClO_4$. However, the 390 cm^{-1} acetone band was shifted gradually (no apparent splitting was observed) to lower frequency as the acetone/Li^+ mole ratio was decreased. The band appeared to reach a limiting value of 380 ± 3 cm^{-1} at acetone/$^{6}LiClO_4$ mole ratio of 4:1, as shown in Figure 6.

Effects of Anion

The anion dependence of some of the solvation bands, notably for the lithium halides, seems to indicate that at least in the system studied, the halides (bromide and chloride) may form a part of the solvation sphere. From electrical conductance studies, it has been postulated (33) that lithium chloride forms unsolvated contact ion pairs, while with lithium iodide the ion pair was said to be formed from fully solvated ions. Lithium bromide represents an intermediate case. The observed frequencies of the solvation bands for the lithium halides are consistent with the above explanation. The frequency of the lithium iodide solvation band is identical with that of lithium perchlorate, lithium thiocyanate, and lithium tetraphenylborate, indicating that the vibration must be that of the cations in the solvent cage. The band shifts to progressively lower frequencies as the iodide ion is replaced first by the bromide and then by the chloride ions. Thus, if our model is correct, the bromide and chloride ions can successfully compete with the acetone

Figure 6. Spectra of solutions of acetone + $^{6}LiClO_4$ in nitromethane.

A. Blank = 1.5 M acetone

B. Acetone/$^{6}LiClO_4$ ratio = 10:1

C. Acetone/$^{6}LiClO_4$ ratio = 6:1

D. Acetone/$^{6}LiClO_4$ ratio = 4:1

E. Acetone/$^{6}LiClO_4$ ratio = 2:1

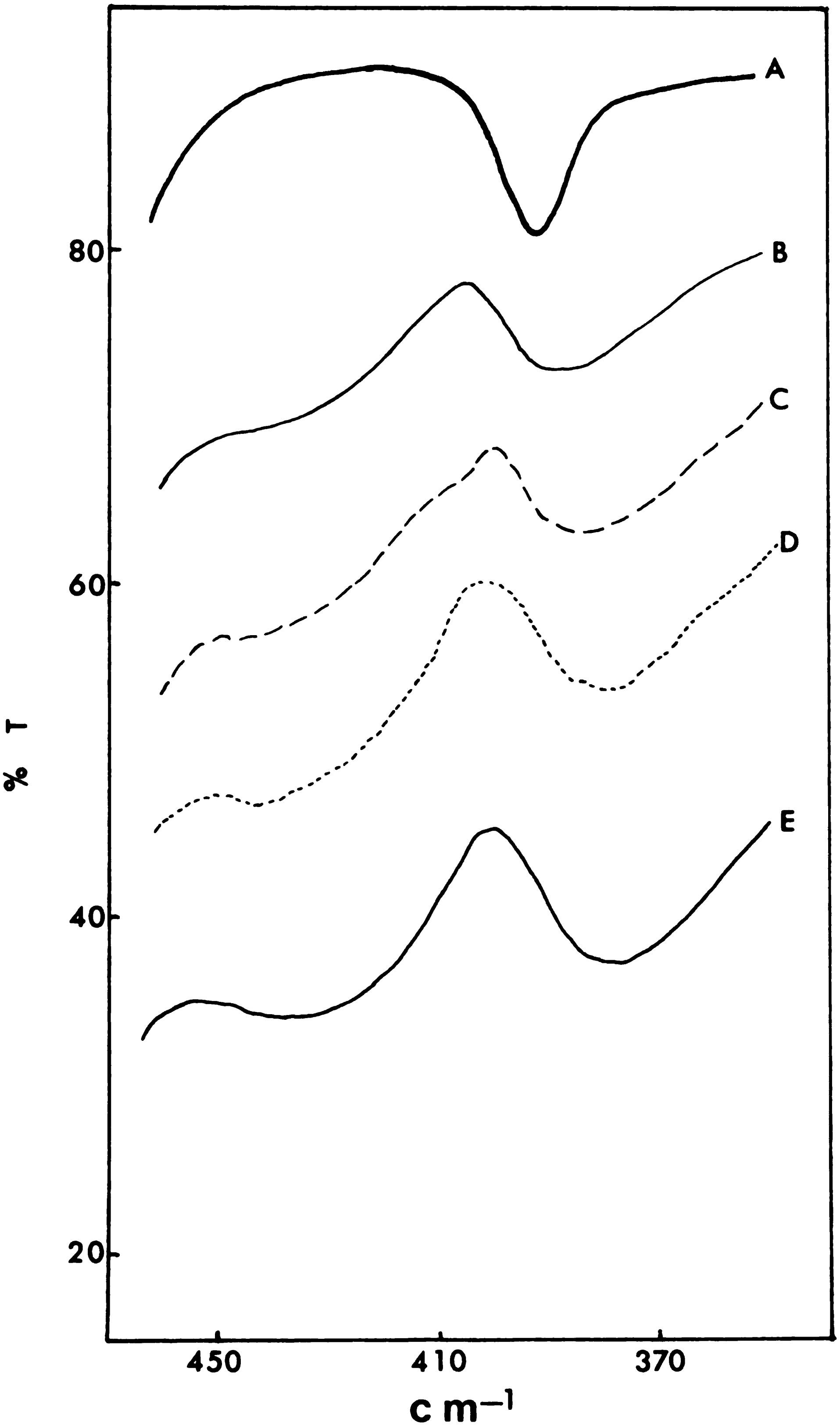


Figure 6.

molecules for the position in the solvent cage even when the concentration of acetone is relatively high as compared with that of the two halide ions.

Recent kinetic study (47) of isotopic exchange of ^{82}Br between lithium bromide and butyl bromide in acetone shows that the exchange rate is very small, and that the lithium bromide ion pairs are unreactive species, indicating that the bromide ion is very strongly bound to the lithium cation.

The fact that the chloride and bromide ions have a strong affinity for the cation is further demonstrated by the following studies. The position and the intensity of the solvation band in 0.5 M lithium perchlorate in acetone solutions were measured as a function of the concentration of added salts, tetrabutylammonium perchlorate, tetrabutylammonium iodide, and tetrabutylammonium bromide. The solvation and the 369 cm^{-1} bands remained practically unchanged upon the addition of 0.4 M tetrabutylammonium perchlorate or 0.4 M tetrabutylammonium iodide. However, upon the addition of tetrabutylammonium bromide, the band shifted progressively from 424 to 412 cm^{-1}, and the 369 cm^{-1} band also shifted to 358 cm^{-1}. The data are given in Table 7. Similar results were obtained with lithium iodide as the solute. Acetone solutions of the various tetrabutylammonium salts did not show any new bands in the measured spectral region. It seems from the above data that the 369 cm^{-1} band is also associated with the cation-solvent vibration.

Symmetrical polyatomic anions, such as the perchlorate ion, have little tendency to form contact ion pairs in the presence of sufficient amounts of a solvating solvent. The Raman band of the perchlorate ion at 935 cm^{-1} remains unchanged when the acetone/$LiClO_4$ mole ratio

Table 7. The Shifting of the 424 cm^{-1} and 369 cm^{-1} Bands

Conc. $LiClO_4$ (M)	Conc. Bu_4NBr (M)	Frequency	
0.54	-	424 $cm^{-1} \pm 3$	369 $cm^{-1} \pm 4$
0.53	0.12	420	368
0.53	0.23	418	368
0.53	0.37	415	364
0.52	0.55	413	362
0.53	0.87	412	358
-	0.30	-	-

is $\geq$ 4. Below this value, however, the band progressively broadens and shifts to higher frequency, and at mole ratio of approximately 1:1, the frequency is at 945 cm^{-1}. These data offer additional evidence that the solvation number of the lithium ion is 4, and that if the system does not contain enough acetone to maintain the solvation shell, the deficiency is made up by the perchlorate ion which then forms a contact ion pair with the cation. The results are shown in Figure 7. It is seen from Figure 7 that parallel with the change in the perchlorate band, there is a change in the appearance of the 789 cm^{-1} (C-C symmetric stretch) Raman band of acetone. As the concentration of lithium is increased, a new band appears at 803 cm^{-1}, representing vibration of the acetone molecule bound to the lithium ion.

Nuclear Magnetic Resonance Mole Ratio Studies

In order to further establish the stoichiometry of the solvated species, mole ratio studies on the acetone-Li^+ system were carried out using proton magnetic resonance spectra (27). Again nitromethane was used as the inert solvent, and the position of the methyl proton resonance of acetone was followed as a function of the acetone/Li^+ ratio. Four studies were performed. In the first study, the acetone concentration was kept constant at 1.5 M and the concentration of lithium perchlorate was varied. The result (Figure 8) shows that there is a definite break in the curve at acetone to salt ratio of 4.3. The position of the methyl proton resonance of nitromethane remains practically unchanged down to about 1:1 mole ratio. In the second study, the lithium perchlorate concentration was kept constant at 0.5 M and the concentration of acetone was varied. Again a break

Figure 7. The 789 cm^{-1} acetone and the 935 cm^{-1} ClO_4^- Raman bands.

A. 3.5 M acetone in nitromethane

B. Acetone/$LiClO_4$ ratio = 6:1

C. Acetone/$LiClO_4$ ratio = 4:1

D. Acetone/$LiClO_4$ ratio = 3:1

E. Acetone/$LiClO_4$ ratio = 2:1

F. Acetone/$LiClO_4$ ratio = ∿1:1

Band intensity semi-quantitative

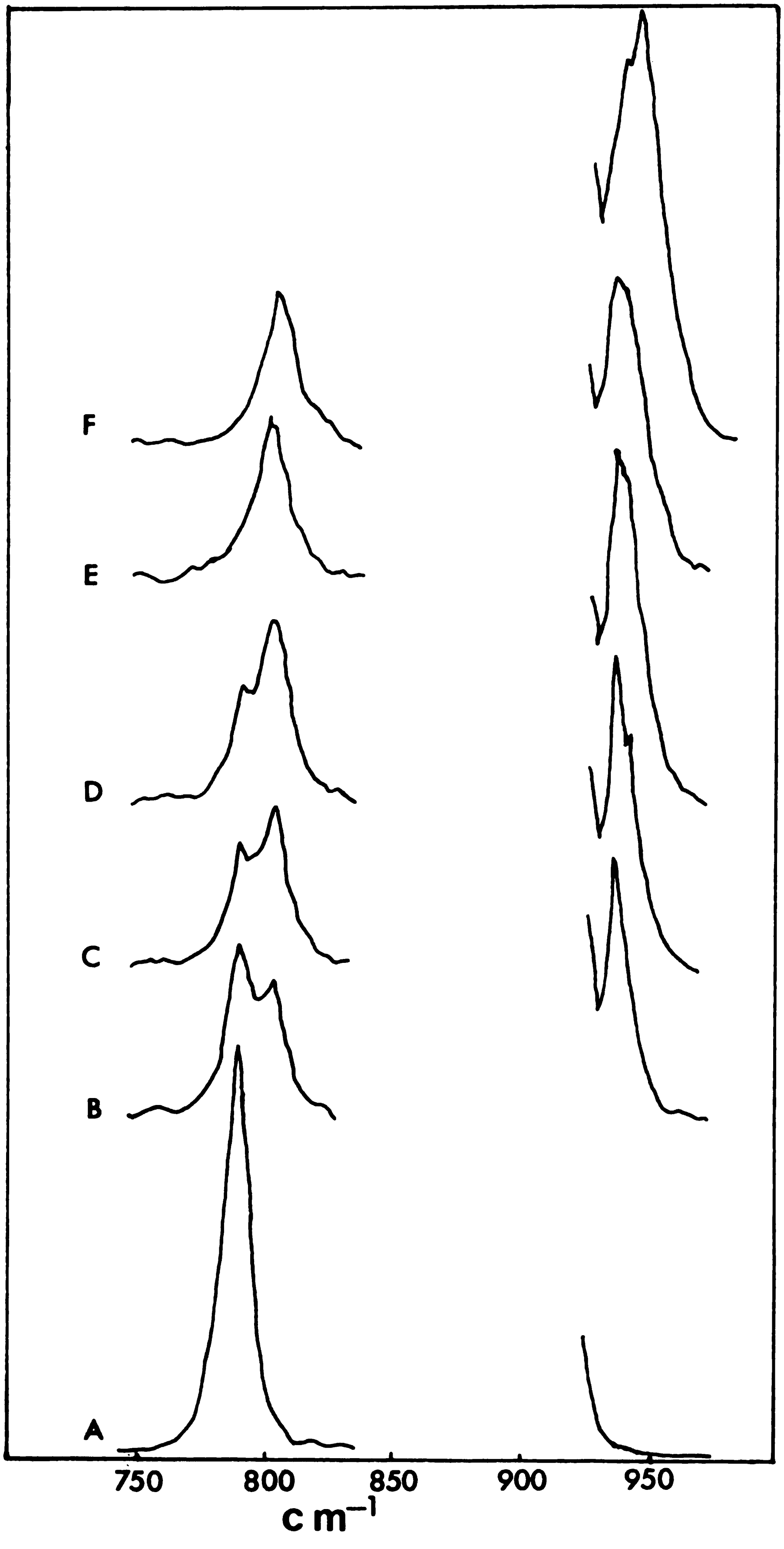
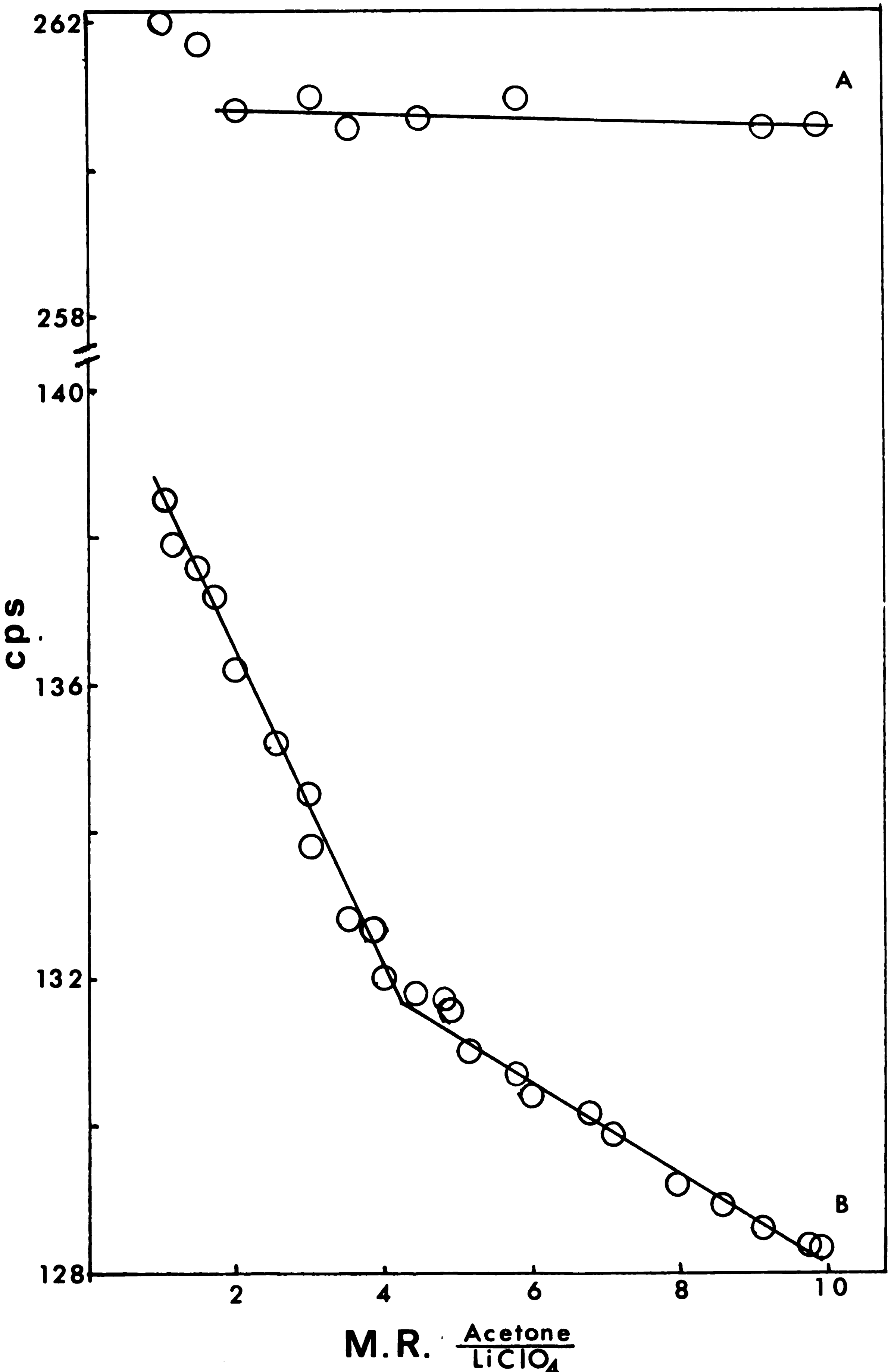


Figure 7.

Figure 8. Chemical shift of the methyl protons of acetone *vs*. acetone/$LiClO_4$ mole ratio. Concentration of acetone = 1.5 M. Concentration of $LiClO_4$ varied. Solvent: nitromethane. A. Nitromethane. B. Acetone.


262
258
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136
132
128
cps
A
B
2
4
6
8
10
M.R. $\frac{\text{Acetone}}{\text{LiClO}_4}$

Figure 8.

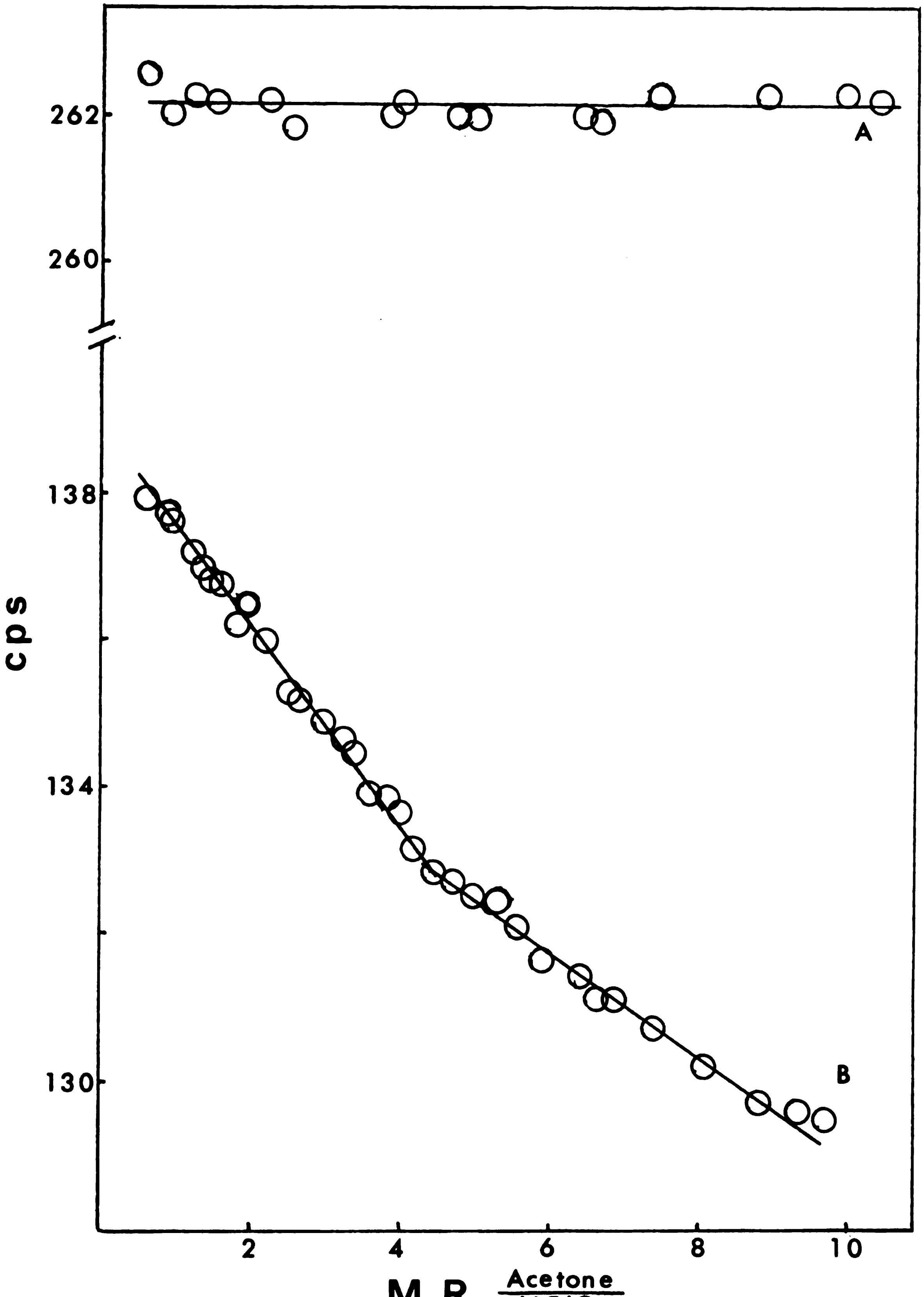
at acetone/$LiClO_4$ mole ratio of 4.4:1 was observed, as shown in Figure 9. Two other studies were carried out using lithium iodide instead of lithium perchlorate. Similar breaks at acetone/LiI mole ratio of 4.4:1 and 4.5:1 were obtained. The results indicate that lithium ion is solvated by four molecules of acetone. It is possible that the deviation from the integral value of 4 are due to the solvation of the anions.

Vapor Pressure Osmometric Measurements

The apparent molecular weights of seven lithium and four sodium salts were measured in acetone. Method I as discussed in Chapter IV was used to calculate the molecular weights. Generally, with the exceptions of the tetraphenylborate salts, the $\Delta R/C$ vs. C (concentration) plots yielded straight lines in the 0.03 to 0.14 M concentration range. For tetraphenylborate, the linear concentration range was 0.02 to 0.10 M. The method of plotting $\Delta R/C$ vs. ΔR (Method II) was used to calculate the apparent molecular weight at each concentration of the salt solutions. The data are given in Tables 8 and 9. The $\Delta R/C$ vs. C_M calibration curve is shown in Figure 10. The calibration curve of $\Delta R/C$ vs. ΔR is similar to Figure 10, except that ΔR is used instead of C. The $\Delta R/C$ vs. C plots for biphenyl, the seven lithium and the four sodium salts are given in Figures 11 to 14. A summary of the results obtained is given in Table 10.

The nonlinearity of the $\Delta R/C$ vs. C plots at concentrations lower than about 0.03 M for most of the salts renders the molecular weights obtained from extrapolation to infinite dilution subject to sizable error (as can be seen from the apparent molecular weight at each concentration vs. concentration plots, Figures 15 to 17). However,

Figure 9. Chemical shift of the methyl protons of acetone vs. acetone/$LiClO_4$ mole ratio. Concentration of $LiClO_4$ = 0.5 M. Concentration of acetone varied. Solvent: nitromethane. A. Nitromethane. B. Acetone.



262
260
138
134
130
cps
A
B
2
4
6
8
10
M.R. $\frac{\text{Acetone}}{\text{LiClO}_4}$

Figure 9.

Table 8. Vapor Phase Osmometry Calibration Data - Benzil in Acetone

Run	Conc (M)	ΔR	$\Delta R/C_m$
I	0.1773	68.93	388.8
	0.1460	57.95	396.9
	0.1147	46.00	401.0
	0.08344	33.93	406.6
	0.06258	25.47	407.0
	0.04172	17.36	416.1
	0.02186	9.14	438.2
	0.01043	4.59	440.1
II	0.1870	72.78	389.2
	0.1603	62.52	390.0
	0.1389	55.12	396.8
	0.1176	46.74	397.6
	0.06412	25.92	404.2
	0.04275	17.57	411.0
	0.03206	13.39	417.7
	0.02137	9.20	430.5
	0.01069	4.72	441.5
III	0.1911	76.02	397.9
	0.1804	71.27	395.2
	0.1486	58.98	396.9
	0.1274	51.30	402.8
	0.1061	42.75	402.8
	0.09022	36.88	408.8
	0.07430	30.33	408.2
	0.05838	24.23	415.0
	0.04777	19.81	414.7
	0.03715	15.67	421.8
	0.02654	11.58	436.3
	0.01592	7.04	442.2

Table 9. Da

L

Run	Con
I	0.1
	0.1
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	0.0
	0.0
	0.0
	0.0
I	0.1
	0.1
	0.0
	0.0
	0.0
	0.0
II	0.
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	0.
	0.
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	0.
	0.

Table 9. Data of Vapor Phase Osmometric Measurements - Biphenyl, Lithium and Sodium Salts

Run	Conc (M)	Conc(g/l)	ΔR	$\Delta R/C_{g/l}$	M_{app}
			Biphenyl		
I	0.1751	27.00	68.84	2.550	153.3
	0.1401	21.60	53.75	2.488	159.9
	0.1138	17.55	45.55	2.595	154.9
	0.08754	13.50	34.35	2.544	159.9
	0.06128	9.450	24.83	2.628	156.8
	0.04377	6.750	17.64	2.613	158.8
	0.01751	2.700	7.68	2.844	153.3
			$LiNO_3$		
I	0.1300	8.960	41.63	4.646	87.0
	0.1056	7.280	35.36	4.857	83.8
	0.08123	5.600	28.34	5.061	81.0
	0.06498	4.480	23.71	5.292	77.9
	0.04874	3.360	28.36	5.464	75.9
	0.03249	2.240	13.40	5.982	70.6
II	0.1304	8.992	41.10	4.571	88.4
	0.1060	7.306	34.96	4.785	85.1
	0.08152	5.620	28.91	5.144	79.7
	0.06522	4.496	23.62	5.254	78.5
	0.04891	3.372	18.53	5.494	75.5
	0.03261	2.248	13.06	5.810	72.7
	0.01630	1.124	7.00	6.228	70.3

Table 9. (C

Run	Conc
I	0.
	0.
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	0
II	
I	
II	

Table 9. (Continued)

Run	Conc (M)	Conc (g/l)	ΔR	$\Delta R/C_{g/l}$	M_{app}
			LiSCN		
I	0.1492	9.700	56.77	5.853	67.8
	0.1193	7.759	45.76	5.898	68.2
	0.09697	6.305	38.13	6.048	67.1
	0.07459	4.850	29.44	6.070	67.5
	0.05221	3.395	21.38	6.297	65.7
	0.03730	2.425	15.48	6.384	65.5
	0.02238	1.455	9.67	6.646	64.8
II	0.1354	8.806	52.45	5.956	67.0
	0.1078	7.009	41.82	5.966	67.7
	0.09560	6.216	37.91	6.099	66.6
	0.07967	5.180	31.64	6.108	66.9
	0.06374	4.144	26.11	6.301	65.2
	0.04780	3.108	20.08	6.461	64.1
	0.03187	2.072	14.01	6.762	62.5
			$LiClO_4$		
I	0.1614	17.168	78.26	4.558	84.7
	0.1311	13.949	63.98	4.587	85.7
	0.1008	10.730	51.47	4.797	83.2
	0.08068	8.584	41.20	4.800	84.2
	0.05650	6.009	30.14	5.016	81.6
	0.03530	3.756	20.27	5.397	76.7
	0.02020	2.146	12.26	5.713	74.3
II	0.1573	16.740	77.55	4.633	83.5
	0.1337	14.229	66.28	4.658	84.1
	0.08653	9.207	45.53	4.945	81.3
	0.06293	6.696	33.56	5.012	81.4
	0.04720	5.022	26.10	5.197	79.1
	0.03147	3.348	18.56	5.544	74.9
	0.01573	1.674	10.08	6.022	71.4

Table 9.

Run	C
I	0 0 0 0 0
II	
I	
II	

Table 9. (Continued)

Run	Conc (M)	Conc (g/l)	ΔR	$\Delta R/C_{g/l}$	M_{app}
			LiCl		
I	0.1030	4.366	27.77	6.361	64.5
	0.08240	3.493	23.20	6.642	62.2
	0.06700	2.840	19.16	6.747	61.5
	0.05150	2.183	15.14	6.935	60.1
	0.03610	1.530	11.23	7.340	58.2
	0.02060	0.873	6.93	7.938	55.2
II	0.1033	4.380	27.98	6.388	64.2
	0.07750	3.285	21.80	6.640	62.3
	0.05683	2.409	16.76	6.957	59.8
	0.04133	1.752	12.82	7.317	57.7
	0.03100	1.314	10.02	7.626	56.4
			LiBr		
I	0.1425	12.375	53.74	4.343	91.7
	0.1173	10.191	45.51	4.466	90.0
	0.1006	8.735	39.45	4.516	89.7
	0.08382	7.280	34.38	4.723	86.2
	0.16705	5.823	27.77	4.769	86.1
	0.05029	4.368	21.86	5.005	82.6
	0.03353	2.912	15.00	5.151	81.3
	0.01676	1.456	8.20	5.632	77.2
II	0.1349	11.712	52.04	4.443	89.8
	0.1111	9.646	44.26	4.587	87.8
	0.09519	8.267	38.43	4.649	87.2
	0.07933	6.890	32.88	4.772	85.5
	0.06346	5.512	27.05	4.908	83.7
	0.04760	4.134	21.02	5.084	81.3
	0.03173	2.756	14.72	5.341	78.5
	0.01587	1.378	7.82	5.674	76.8

Table 9. (

Run	Co
I	0.
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II	0.
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	0.
	0.
	0.
	0.
I	0.
	0.
	0.
	0.
	0.
	0.
	0.
II	0.
	0.
	0
	0.
	0.
	0.
	0.
	0.

Table 9. (Continued)

Run	Conc (M)	Conc (g/l)	ΔR	$\Delta R/C_{g/l}$	M_{app}
			LiI		
I	0.1449	19.390	66.10	3.409	115.0
	0.1177	15.760	55.64	3.530	112.4
	0.09959	13.330	46.95	3.522	113.8
	0.07243	9.695	36.95	3.811	106.5
	0.05432	7.271	28.40	3.906	105.0
	0.03622	4.848	20.64	4.257	97.2
	0.018109	2.424	11.37	4.691	90.9
II	0.1375	18.400	62.81	3.414	115.4
	0.1203	16.099	56.42	3.505	113.3
	0.1031	13.800	49.57	3.592	111.4
	0.08591	11.500	42.76	3.718	108.5
	0.06873	9.200	35.90	3.902	104.2
	0.05155	6.901	27.44	3.976	103.2
	0.03436	4.599	19.18	4.171	99.5
	0.01718	2.300	10.71	4.657	92.0
			$LiBPh_4$		
I	0.1043	34.016	64.51	1.896	207.5
	0.07821	25.512	48.75	1.911	209.6
	0.06518	21.262	41.38	1.946	207.6
	0.05214	17.008	34.54	2.031	200.6
	0.03911	12.758	25.95	2.034	202.2
	0.02607	8.504	18.21	2.141	193.8
	0.01304	4.254	9.48	2.228	193.4
II	0.1147	37.415	69.50	1.857	210.2
	0.09447	30.816	58.26	1.891	209.5
	0.07422	24.211	45.97	1.899	211.6
	0.05978	19.500	38.63	1.981	204.4
	0.03985	12.999	26.84	2.065	199.1
	0.02699	8.804	18.50	2.101	197.5
	0.01993	6.501	14.00	2.154	195.5
	0.01350	4.404	9.59	2.178	197.8

Table 9. (Continued)

Run	Conc (M)	Conc(g/l)	ΔR	$\Delta R/C_{g/l}$	M_{app}
			$NaBPh_4$		
I	0.1220	41.76	80.42	1.926	200.1
	0.1005	34.39	65.61	1.908	205.4
	0.07895	27.02	52.16	1.930	206.7
	0.06460	22.11	42.04	1.901	212.4
	0.05024	17.194	33.56	1.952	209.0
	0.03589	12.283	24.01	1.956	210.8
	0.02153	7.370	15.06	2.043	205.1
	0.01436	4.913	10.19	2.074	207.0
II	0.08615	29.48	56.03	1.901	208.9
	0.06627	22.68	44.62	1.967	204.5
	0.04639	15.877	31.59	1.990	205.6
	0.03314	11.342	22.36	1.972	209.5
	0.01325	4.535	9.71	2.142	201.3
			$NaClO_4$		
I	0.01505	18.429	71.64	3.887	100.2
	0.1239	15.172	61.02	4.022	98.1
	0.1062	13.004	52.96	4.072	97.8
	0.08853	10.840	45.18	4.168	96.4
	0.07082	8.672	36.45	4.203	96.7
	0.05312	6.504	28.08	4.317	95.1
	0.03541	4.336	19.50	4.497	92.2
	0.01771	2.168	10.77	4.968	86.2
II	0.1659	20.32	78.52	3.864	99.9
	0.1481	18.130	70.57	3.892	100.2
	0.1219	14.930	60.54	4.055	97.4
	0.1045	12.797	52.40	4.095	97.5
	0.08709	10.664	44.35	4.159	96.8
	0.06968	8.532	36.35	4.260	95.4
	0.05226	6.399	28.05	4.384	93.6
	0.04006	4.906	21.96	4.476	92.4
	0.02177	2.666	13.22	4.959	85.2

Table 9. (

Run	Con
I	0.1
	0.1
	0.0
	0.0
	0.0
	0.0
II	0.
	0.
	0.
	0.0
	0.0
	0.0
I	0.
	0.
	0.
	0.
	0.
	0.
	0.
	0.
II	0.
	0.
	0.
	0.
	0.
	0.
	0.

Table 9. (Continued)

Run	Conc (M)	Conc (g/l)	ΔR	$\Delta R/C_{g/1}$	M_{app}
			NaI		
I	0.1292	19.375	63.06	3.255	121.0
	0.1016	15.224	51.21	3.365	119.0
	0.08308	12.455	42.18	3.387	119.2
	0.06462	9.688	33.57	3.465	117.7
	0.04616	6.920	25.77	3.724	110.5
	0.02770	4.153	16.54	3.983	104.7
II	0.1491	22.36	71.25	3.186	122.4
	0.1228	18.410	58.54	3.180	124.6
	0.1017	15.290	51.14	3.345	119.3
	0.07017	10.520	36.32	3.452	117.7
	0.04386	6.575	24.26	3.690	111.7
	0.01754	2.630	10.97	4.171	102.5
			NaSCN		
I	0.1555	12.608	58.10	4.608	85.9
	0.1372	11.124	52.22	4.694	85.0
	0.1189	9.640	47.11	4.887	82.0
	0.09146	7.415	37.12	5.006	81.1
	0.06402	5.191	27.57	5.311	77.3
	0.04573	3.708	20.68	5.577	74.2
	0.02744	2.225	13.27	5.964	70.8
	0.01463	1.186	7.75	6.532	66.7
II	0.1613	13.078	60.98	4.663	84.6
	0.1371	11.116	52.38	4.712	84.7
	0.1129	9.156	44.55	4.867	82.7
	0.08873	7.194	35.35	4.914	82.8
	0.06453	5.232	27.43	5.243	78.4
	0.04033	3.270	18.32	5.602	74.1
	0.01613	1.308	8.15	6.231	69.8

Figure 10. The $\Delta R/C_m$ vs. C_m calibration plot. Benzil in acetone.

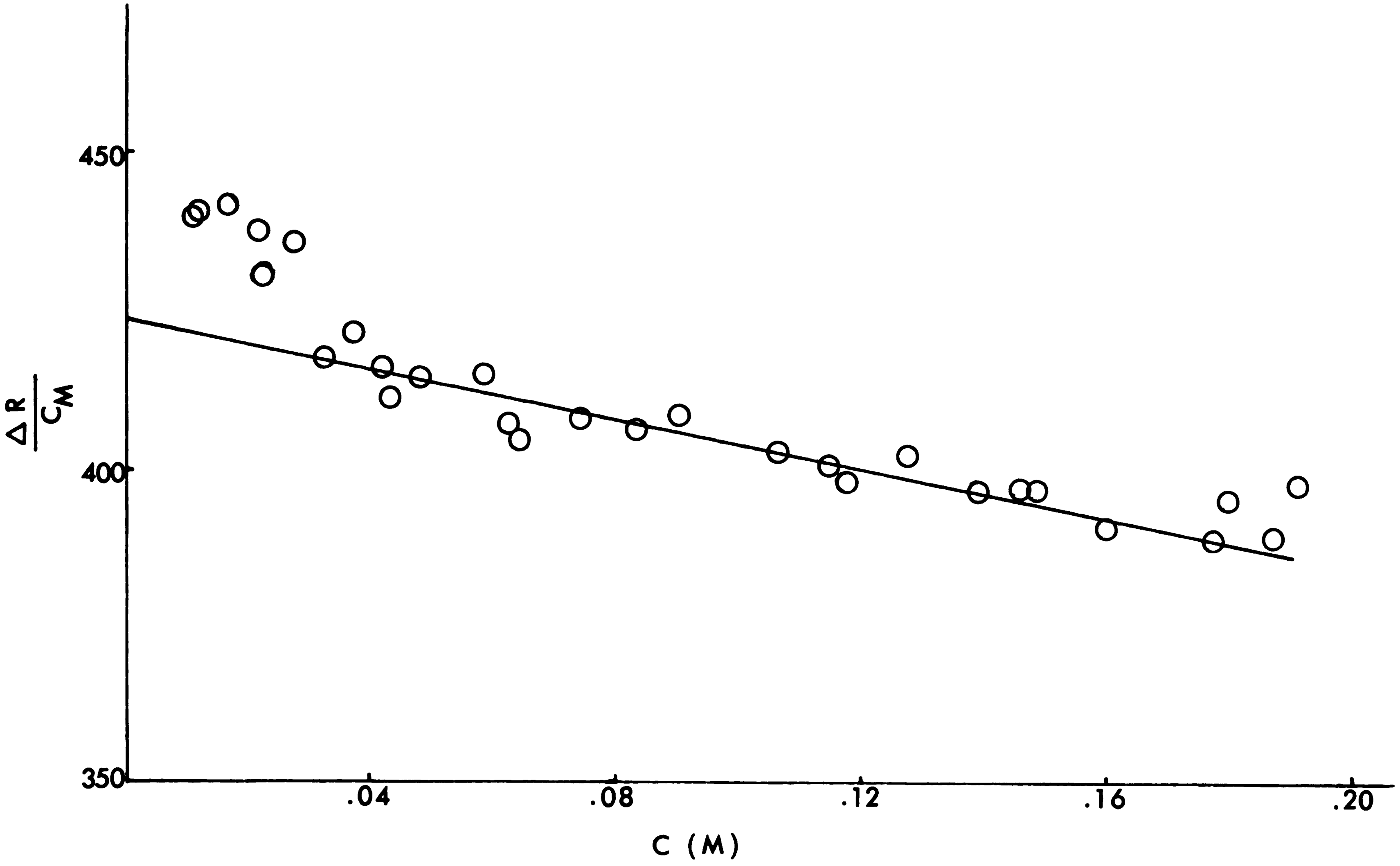

Figure 10.

Figure 11. The $\Delta R/C_{g/l}$ vs. $C_{g/l}$ plots for (A) LiCl. (B) LiSCN. (C) $LiNO_3$.

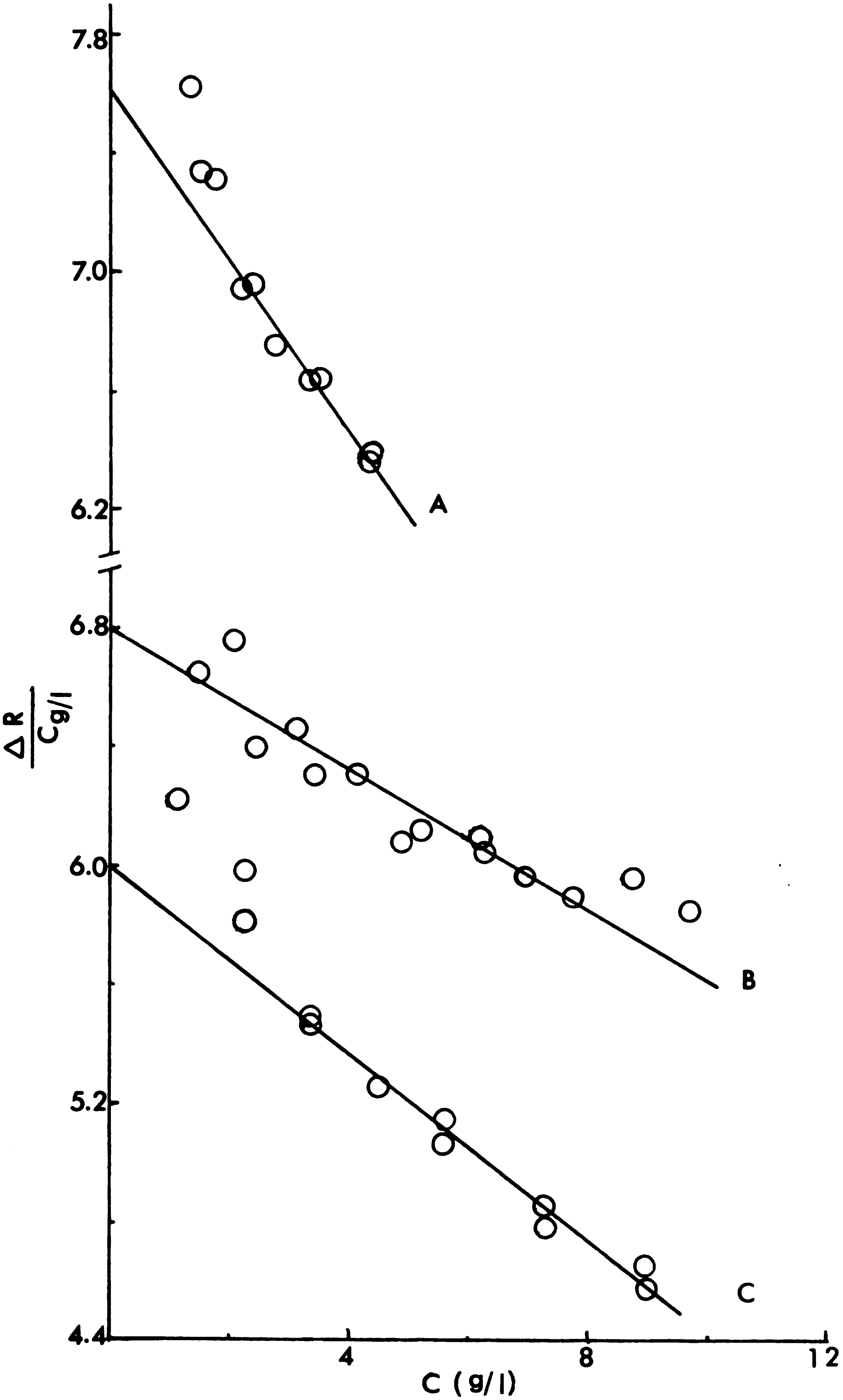

Figure 11.

Figure 12. The $\Delta R/C_{g/l}$ *vs*. $C_{g/l}$ plots for (A) Biphenyl. (B) $LiBPh_4$. (c) $NaBPh_4$.

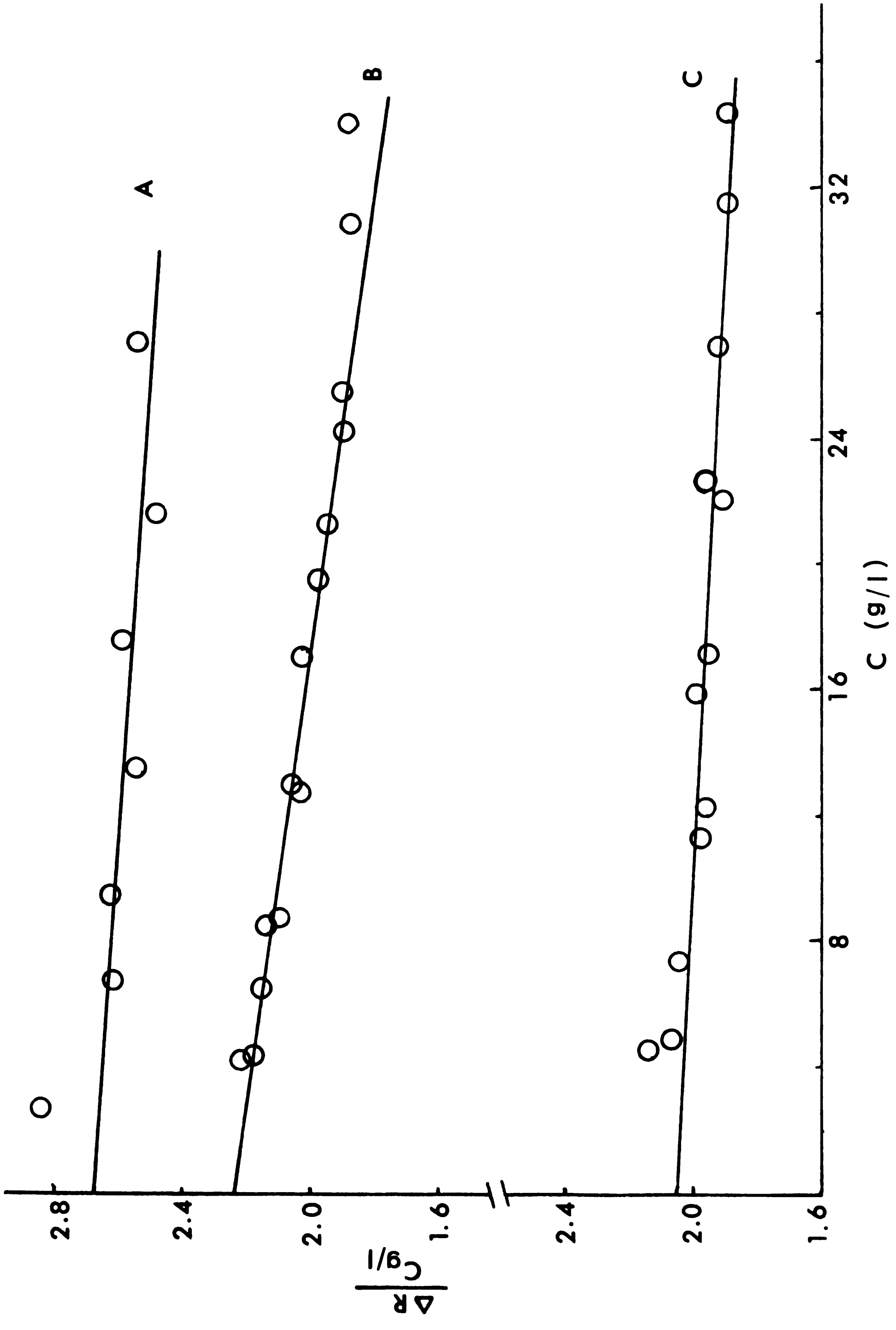

Figure 12.

Figure 13. The $\Delta R/C_{g/l}$ vs. $C_{g/l}$ plots for (A) NaSCN. (B) $LiClO_4$. (C) LiBr.

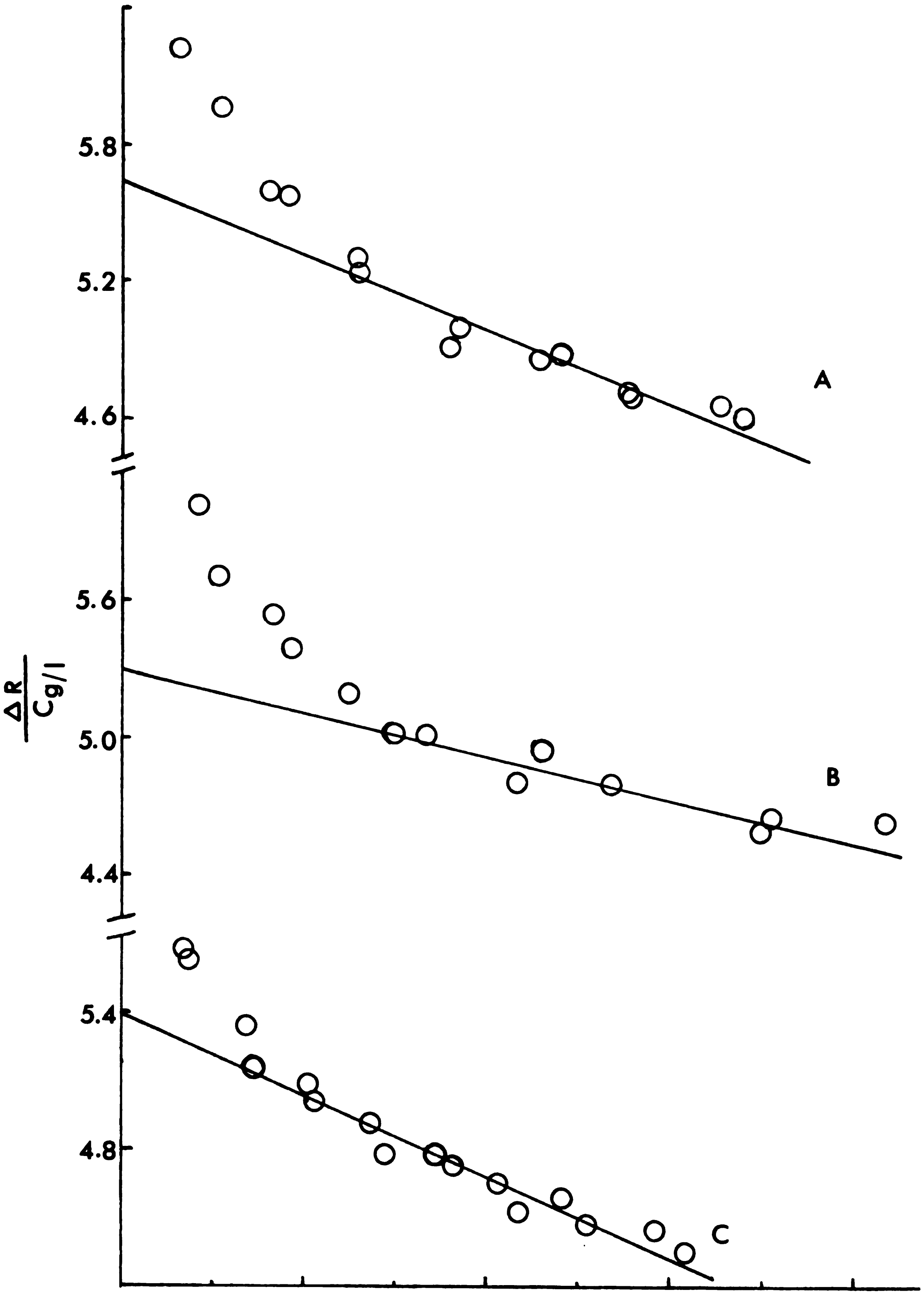

Figure 13.

Figure 14. The $\Delta R/C_{g/1}$ vs. $C_{g/1}$ plots for (A) $NaClO_4$. (B) LiI. (C) NaI.

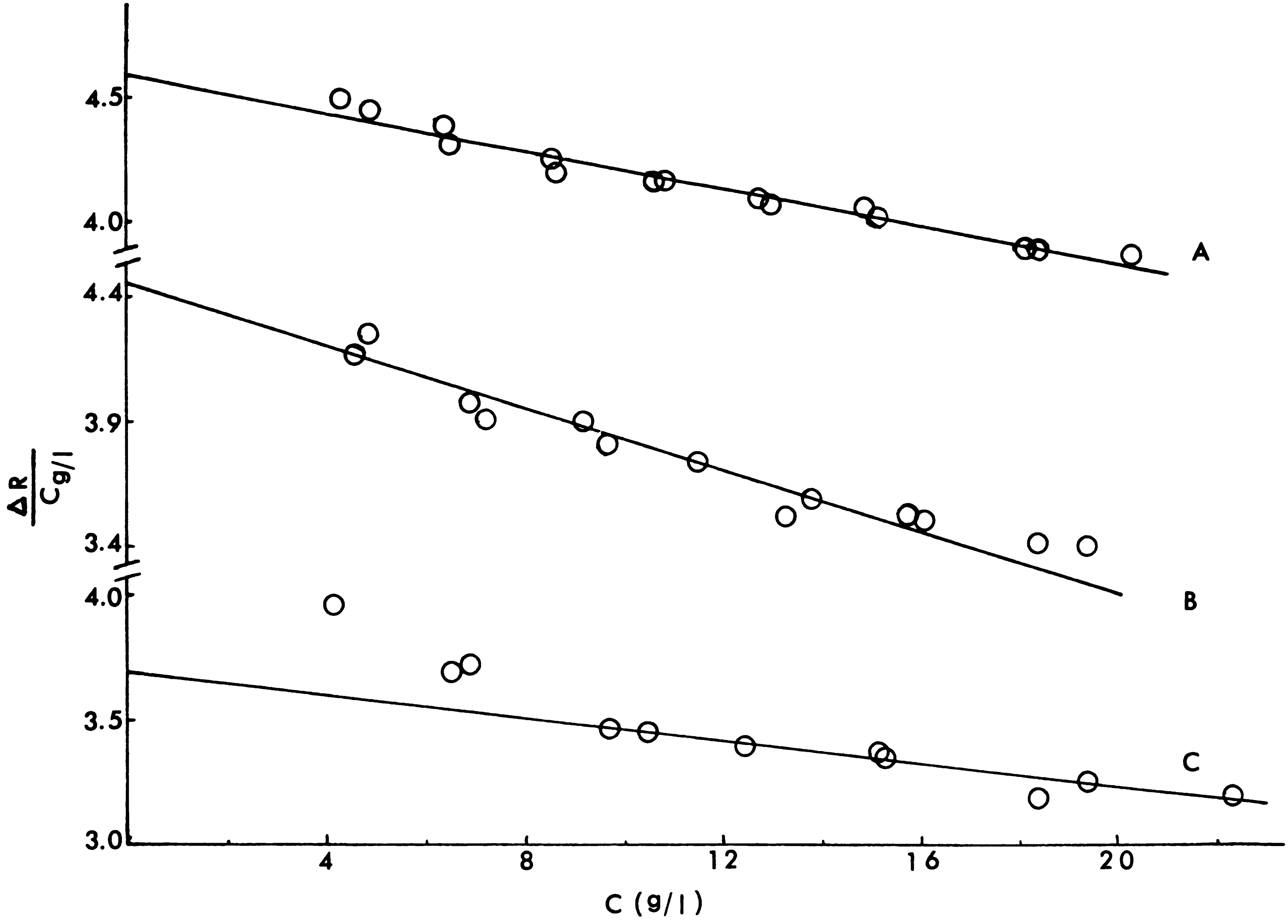

Figure 14.

Table 10.

Salt
LiCl
LiBr
LiI
$LiNO_3$
LiSCN
$LiClO_4$
$LiBPh_4$
NaI
NaSCN
$NaClO_4$
$NaBPh_4$
Bipheny

---

*In the

Table 10. The Apparent Molecular Weights of Alkali Metal Salts in Acetone

Calibration Constant $K_m = 424$

Salt	$(\Delta R/C_{g/l})_{C=0}$	Mol. Wt. (apparent)	Mol. Wt. (real)	M_{app}/M_{real}	Linear Conc Range*
LiCl	7.60	55.8	42.4	1.32	0.03 -- 0.10
LiBr	5.40	78.5	86.9	0.90	0.03 -- 0.14
LiI	4.46	95.1	133.8	0.77	0.03 -- 0.14
$LiNO_3$	6.00	70.7	68.9	1.03	0.04 -- 0.13
LiSCN	6.80	52.4	65.0	0.96	0.03 -- 0.13
$LiClO_4$	5.30	82.3	106.4	0.77	0.04 -- 0.14
$LiBPh_4$	2.24	189.3	326.2	0.58	0.01 -- 0.09
NaI	3.70	114.6	149.9	0.76	0.04 -- 0.15
NaSCN	5.65	75.0	81.1	0.92	0.04 -- 0.15
$NaClO_4$	4.59	92.2	122.4	0.75	0.04 -- 0.15
$NaBPh_4$	2.06	205.8	342.2	0.60	0.01 -- 0.10
Biphenyl	2.68	158.2	154.2	1.03	0.02 -- 0.14

*In the ΔR/C vs. C (unit g/l) plots.

Figure 15. The apparent molecular weights (M_{app}) vs. molar concentration plots. (A) $LiNO_3$. (b) LiI. (C) LiBr. (D) LiCl.

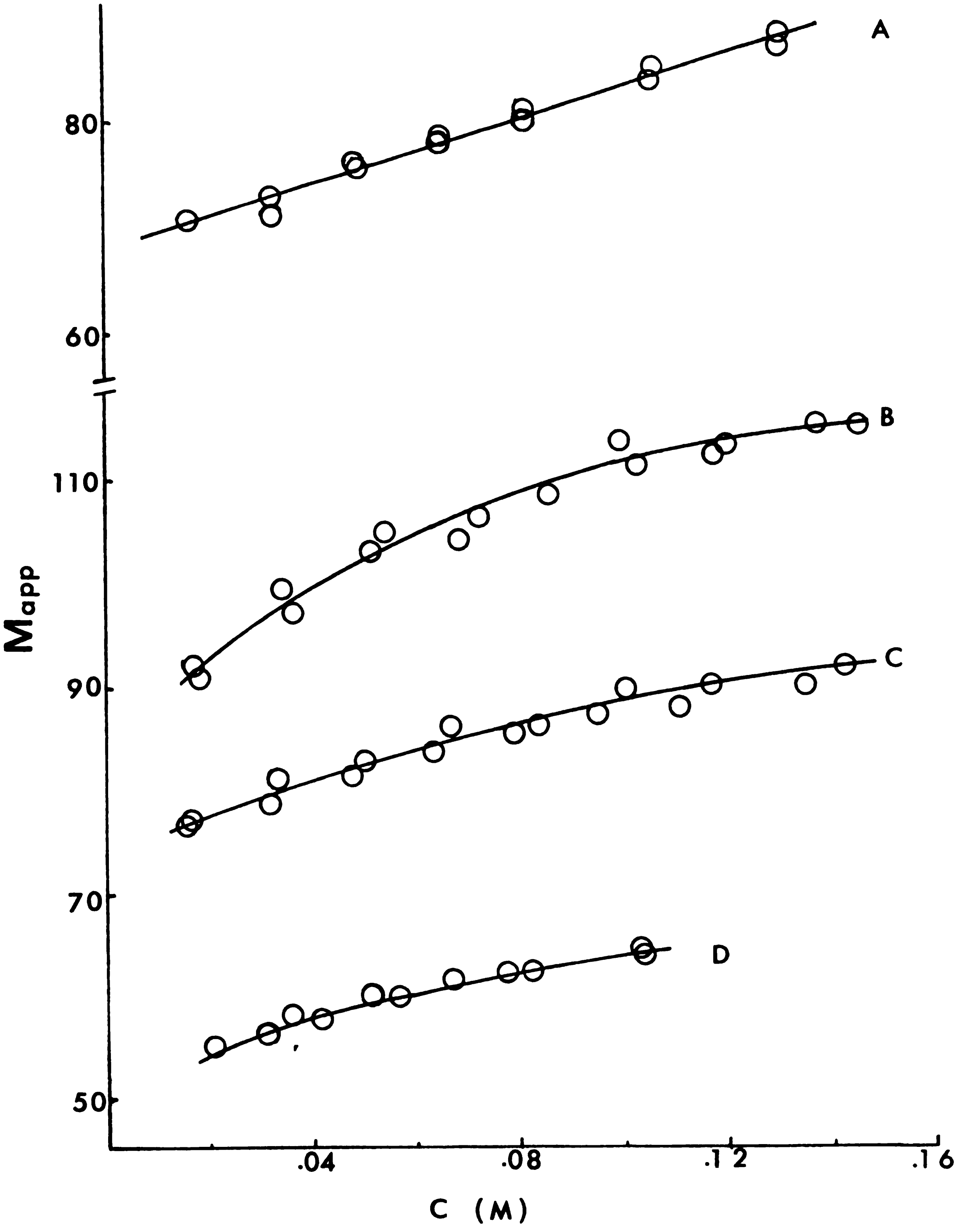

Figure 15.

Figure 16. The apparent molecular weights (M_{app}) vs. molar concentration plots. (A) $LiBPh_4$. (B) Biphenyl. (C) $LiClO_4$. (D) LiSCN.

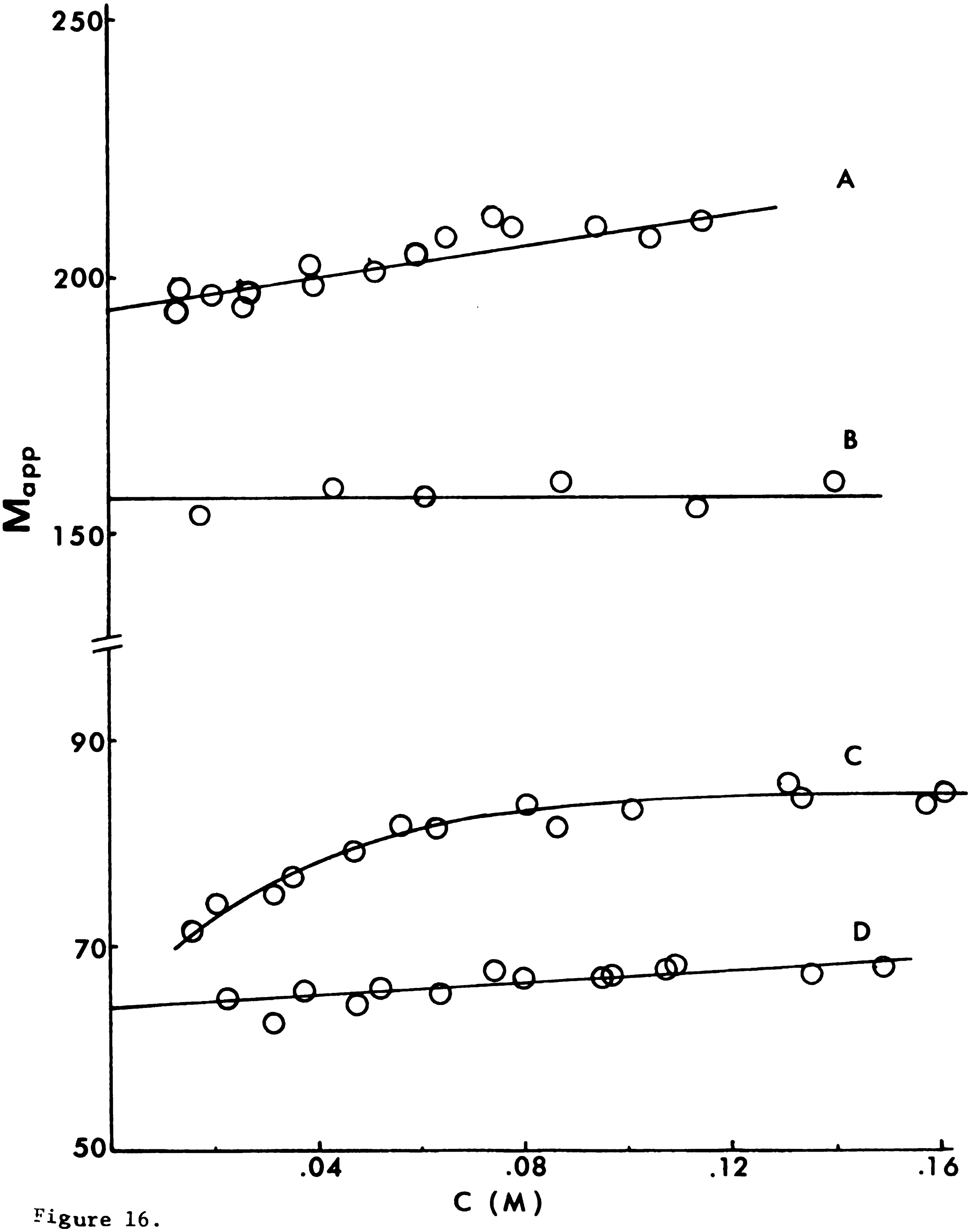

Figure 16.

Figure 17. The apparent molecular weights (M_{app}) vs. molar concentration plots. (A) $NaBPh_4$. (B) NaI. (C) $NaClO_4$. (D) NaSCN.

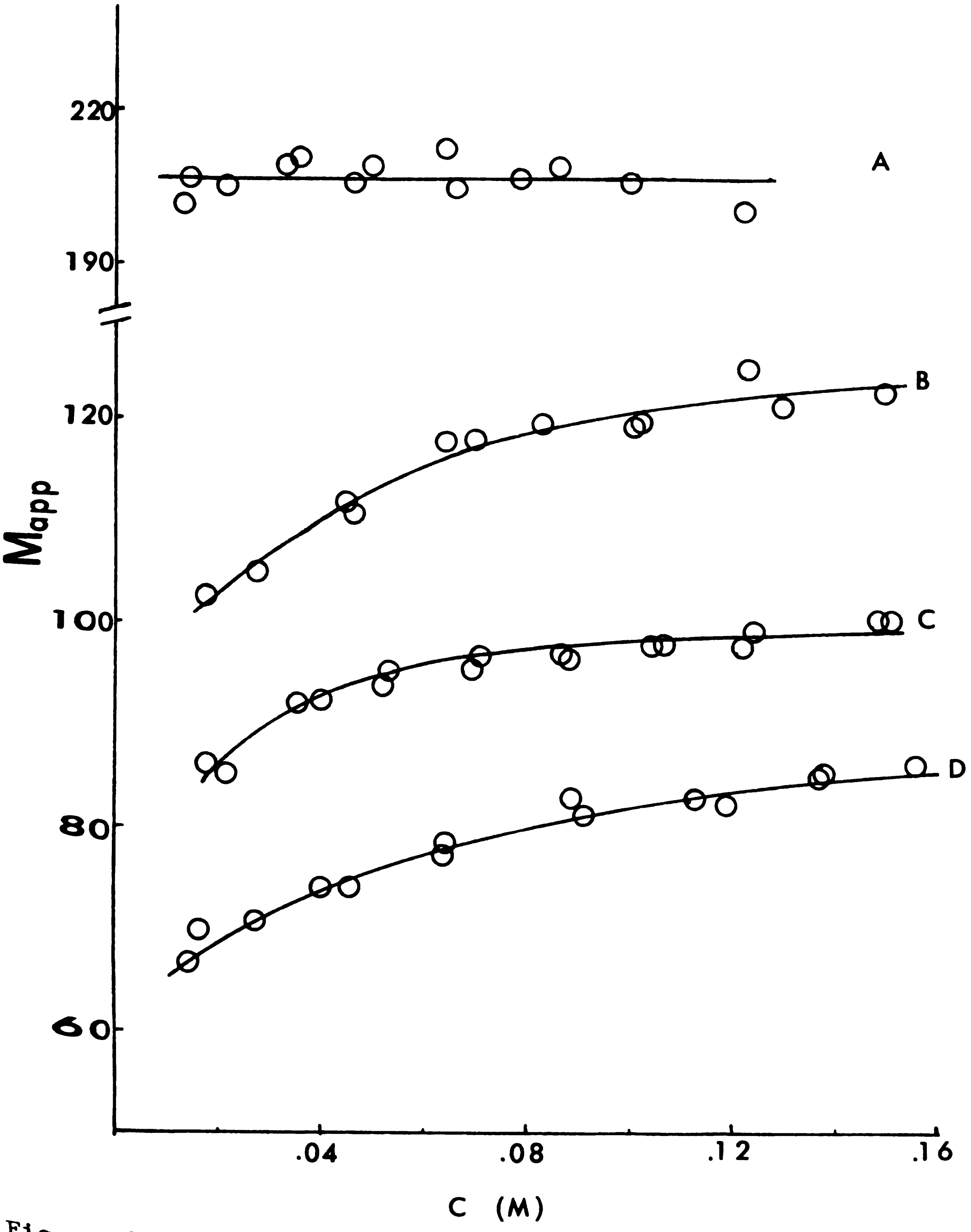

Figure 17.

in the 0.03 to 0.14 M concentration range, a qualitative comparison of the apparent molecular weights of the various salts may be of significance.

From the apparent molecular weights it is seen that among the lithium salts, the tetraphenylborate is the most dissociated, the iodide and the perchlorate appear to be less dissociated, and no appreciable dissociation is observed for the nitrate, thiocyanate and the bromide. Apparently, higher aggregates (ionic or molecular) are present in appreciable amount for lithium chloride.

Sodium iodide, sodium perchlorate and sodium tetraphenylborate are also appreciably dissociated, with greatest dissociation being observed for the tetraphenylborate. Some association is observed, however, in the sodium thiocyanate solutions.

From the greater dissociation of lithium tetraphenylborate, lithium iodide, lithium perchlorate and the sodium salts, we would expect that the above electrolytes exist in solutions mainly as solvent-separated ion pair. The molecular weights for lithium nitrate, lithium thiocyanate and lithium bromide indicate no appreciable dissociation in the concentration range studied. Even in these cases, solvent separated ion pairs cannot be ruled out for the three salts, especially for the polyatomic anion salts.

From the apparent molecular weight, it is reasonable to assume that, in addition to ion pairs, appreciable higher ionic or molecular aggregates exist for lithium chloride in acetone solution. Thus the far infrared band for the lithium chloride in acetone may arise from vibrations of contact ion pair, or solvated contact ion pair, or other solvated species of higher aggregates. The fact that the chloride and the bromide ions do form strong bonds with lithium ion have been shown by the low ion pair dissociation constants from conductance (33) and kinetic isotopic exchange studies (47). Thus the results from vapor pressure osmometric measurements agree with the trends observed from the various studies.

With the exceptions of biphenyl and sodium tetraphenylborate, the apparent molecular weights of all the salts studied show some degree of concentration dependence. The apparent molecular weight at each salt concentration _vs_. molar concentration plots for the eleven salts studied are shown in Figures 15 to 17. Besides biphenyl and sodium tetraphenylborate, the salts lithium tetraphenylborate and lithium thiocyanate also show very small degrees of concentration dependence of their apparent molecular weights.

(B) Acetic Acid

Preliminary investigations indicated that acetic acid is quite transparent in the 430-250 cm^{-1} spectral region as well as below 150 cm^{-1}. It is opaque between 250 and 150 cm^{-1}. The lithium salts are quite soluble in acetic acid. Some sodium salts are also slightly soluble. Among the common salts of other alkali metals only the fluorides have sufficient solubilities for spectral measurements.

The frequencies of the far infrared solvation bands of lithium salts, together with those of potassium fluoride, rubidium fluoride, cesium fluoride and tetramethylammonium fluoride are shown in Table 11. The values are given for the averages of at least three runs. The concentration range studied was 0.1 to 1.5 M. The intensities of the observed bands were proportional to the salt concentrations.

Table 11. Solvation Bands of the Alkali Metal Salts in Acetic Acid Solutions (cm^{-1})

Salt	CH_3COOH	CD_3COOD
LiCl	390 ± 4	364 ± 5
LiBr	391	367
LiI	392	368
$LiNO_3$	390	366
LiSCN	391	366
$LiClO_4$	390	366
$LiBPh_4$	389	362
^6LiCl	405 ± 5	
^6LiBr	408	
^6LiI	410	
$^6LiNO_3$	407	
$^6LiClO_4$	405	
KF	281 ± 10	
RbF	283	
CsF	281	
$(CH_3)_4NF$	278	

It is interesting to note that all the lithium salts show a band at 390 ± 4 cm^{-1} irrespective of the nature of the anion. In acetone solutions the band frequencies of the lithium salts with polyatomic anions were also found to be independent of the anion but the halides showed bands at slightly different frequencies, indicating the possible formation of contact ion pairs. It seems, therefore, that in acetic acid solutions contact ion pairs are not formed by lithium salts to any appreciable extent although, of course, due to the low dielectric constant of the solvents the electrolytes exist largely in the form of solvent-separated ion pairs. The low frequency of the lithium - acetic acid solvation band, as compared with other solvents (e.g., 429 cm^{-1} in dimethyl sulfoxide (1), 425 cm^{-1} in acetone, etc.) seem to reflect lower energy of interaction between acetic acid and the lithium ion. The fact that the frequency of this band changed upon isotopic substitution (^6Li and CD_3COOD) substantiates the assumption that the band is due to the cation-solvent vibration.

The shifts with isotopic substitution are similar to those observed with acetone. Application of the same Hook's law calculation to acetic acid predicts a shift of 28 cm^{-1} with the substitution of ^6Li salts in place of the ^7Li salts. Experimentally the shift is found to be approximately 15 cm^{-1}. Similarly, Hook's law calculation of the effect of substitution of deuterated solvent predicts a shift of less than 2 cm^{-1}. Experimentally a large shift of about 24 cm^{-1} is observed.

The effect of water on the far-infrared solvation bands was examined by the gradual addition of water to solutions of lithium perchlorate. The results are shown in Figure 18. It is seen that

Figure 18. The effect of water on the solvation band of $LiClO_4$ in acetic acid solution.

A. Pure acetic acid.

B. 0.7 M $LiClO_4$ in acetic acid. Water content = 0.06% (with no addition of water).

C. 0.6 M $LiClO_4$ in acetic acid. Water content = 1.1%.

D. 0.6 M $LiClO_4$ in acetic acid. Water content = 2.3%.

E. 0.6 M $LiClO_4$ in acetic acid. Water content = 4.7%.

The same cell was used to obtain B, C, D and E. A was obtained from a different cell.

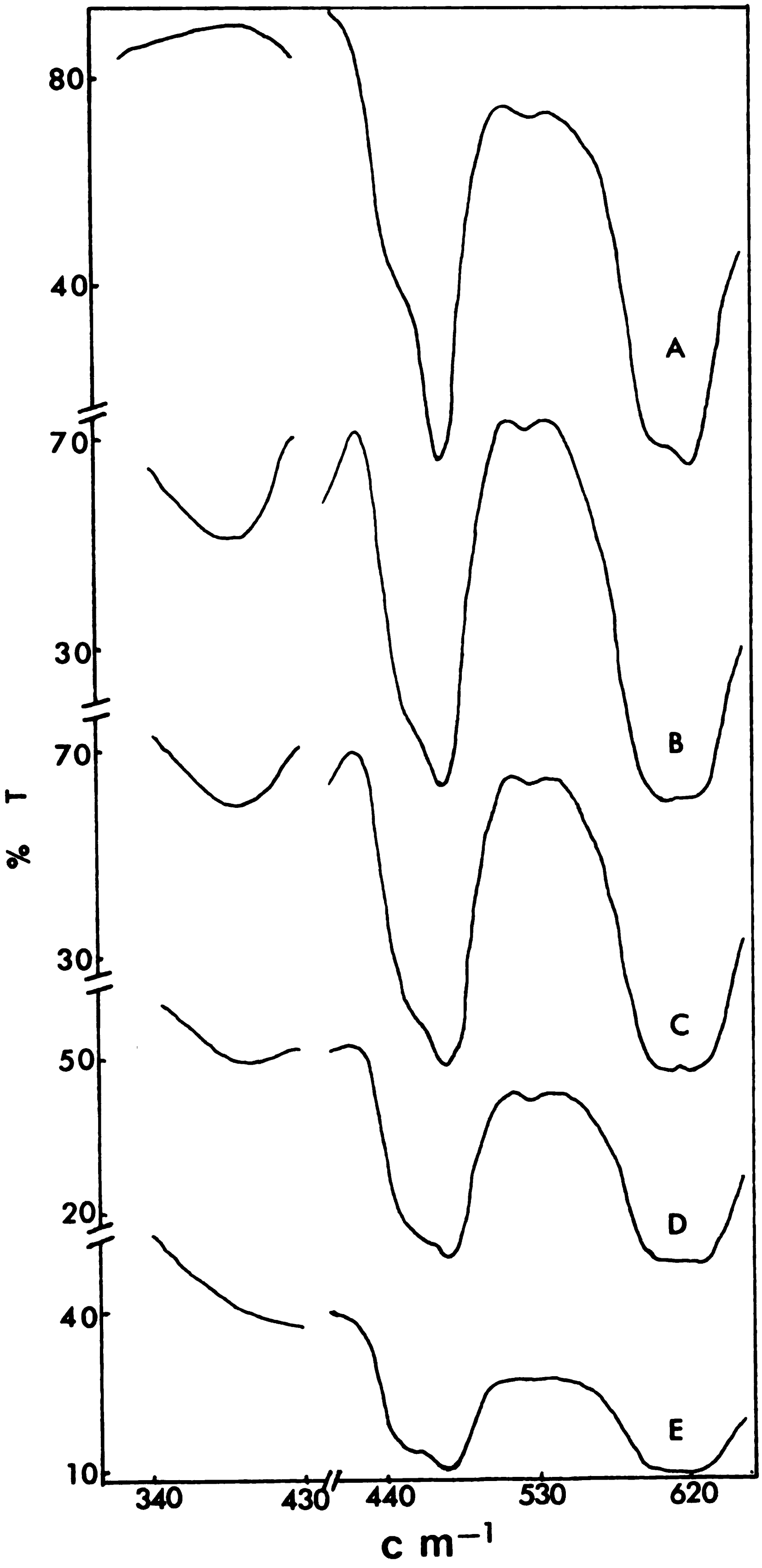

Figure 18.

the position of the solvation band does not change upon the addition of small amounts of water. Even at 2% water, the band can still be vaguely distinguished. However, due to water absorption, the baseline increases with increasing water content. The solvation band practically disappeared at water content above about 2.5%. Since most of the measurements were done with 0.5 M solution of salts and the combined water content of salt and solvent at this concentration was less than 0.1%, the effect of this small amount of water would be negligible.

The solvation bands of sodium and ammonium ions usually occur at $\sim$200 cm^{-1}. Since the solvent is opaque in this region these bands could not be observed. The solvation bands of rubidium and cesium ions occur below 150 cm^{-1}. The spectra of the respective fluorides were measured in this region but the solvation bands were not found, indicating that the solvent-cation interaction is quite weak, at least by comparison with that found in other solvents studied thus far. On the other hand, a broad band was observed at $\sim$280 cm^{-1} for both fluorides as well as for solutions of potassium and tetramethylammonium fluorides. Thus, unlike the solvation bands studied thus far, the 280 cm^{-1} band must be due to fluoride anion - solvent vibration. Acetic acid is a strongly hydrogen-bonding solvent and since the fluoride ion is particularly susceptible to the formation of hydrogen-bond, it is not surprising that this interaction is manifested by the anion solvation band. The other halide anions must also undergo some hydrogen-bonding with the solvent, although to a lesser extent than the fluoride ion and, therefore, it seems reasonable to assume that the lithium halides in acetic acid solutions do not form strong contact ion pairs.

A one molar hydrogen fluoride solution in acetic acid was prepared by mixing acetic anhydride with a stoichiometric amount of aqueous 48% hydrofluoric acid. The spectrum of the solution was similar to that of pure acetic acid. The 280 cm^{-1} fluoride anion - acetic acid solvation band observed for other fluorides was conspicuously absent, and no new band was detected in the 600—250 cm^{-1} spectral region. Since hydrogen fluoride forms very strong hydrogen-bonds within itself and thus is highly associated, it is likely that the fluoride anion in hydrogen fluoride does not interact appreciably with the acetic acid hydroxyl proton, and thus the fluoride anion solvation band can not be observed.

Raman spectra in the 3000-150 cm^{-1} spectral region were also obtained of the lithium perchlorate, bromide, nitrate and of rubidium fluoride and cesium fluoride solutions in acetic acid in the 0.6-2.0 M concentration range. The 390 cm^{-1} lithium - acetic acid and 280 cm^{-1} fluoride - acetic acid solvation bands were not observed. Thus the bands are Raman-inactive and, therefore, the solvent - ion interactions must be essentially electrostatic.

Attempts to measure the apparent molecular weights of the electrolytes in acetic acid by vapor pressure osmometry were unsuccessful. The thermistors of the osmometer could not be balanced with pure solvent, due to excessive drifting. The low vapor pressure of the solvent at 37°C may produce too small a temperature difference to allow meaningful measurements.

(C) Dimethyl Sulfoxide

Attempts to run vapor pressure osmometry measurements using dimethyl sulfoxide as solvent were unsuccessful. As in the case of acetic acid, the thermistors of the osmometer could not be properly balanced with the pure solvent. The vapor pressure of dimethyl sulfoxide at 37°C is probably too low to give meaningful readings.

(D) Tetrahydrofuran

Far Infrared Studies

Tetrahydrofuran is a relatively good solvent for far infrared solvation studies. It has a good spectral window with only one absorption band at 283 cm^{-1} in the 600 to 100 cm^{-1} spectral range. The band is shifted to 235 cm^{-1} in tetrahydrofuran-d_8. Most of the common lithium salts and some of the sodium salts are quite soluble in the solvent.

The far infrared spectra of six lithium salts and one sodium salt in tetrahydrofuran solutions were measured. In all cases, a broad band, which has been assigned to alkali ion vibration, appeared in the spectrum of each salt solution. The frequency for the lithium perchlorate band, which has not been determined previously, was 404 ± 3 cm^{-1}. The frequencies of the solvation bands for other salts, with the exception of lithium iodide, agree with those of Edgell, _et_ _al_., to within 2 cm^{-1} (see Chapter II). The spectra of several lithium salts in tetrahydrofuran-d_8 solutions were also measured. The data are given in Table 12.

From Table 12, it is seen that the substitution of deuterated solvent has practically no effect on the frequency of the lithium chloride band in tetrahydrofuran solution. The shifting of the lithium bromide band frequency is also within the experimental uncertainty. The band frequency of the lithium perchlorate

Table 12. Frequencies (cm^{-1}) of Alkali Ion Vibrations in Tetrahydrofurans

Salt	Tetrahydrofuran	Tetrahydrofuran-d_8
LiCl	389 ± 3	389 ± 3
LiBr	380	377
LiI	381	
$LiClO_4$	404	396
$LiNO_3$	408	
$LiBPh_4$	412	
NaI	182	

solution shifted from 404 cm^{-1} in tetrahydrofuran to 396 cm^{-1} in tetrahydrofuran-d_8, a shift of 8 cm^{-1}, which is beyond the experimental uncertainty and shows that the solvent participates in the vibration. The observed constancy of the lithium chloride band frequency upon substitution of the deuterated solvent may be fortuitous; however, it may also indicate that the solvent does not participate in the vibration of lithium chloride in tetrahydrofuran solution.

Ferraro, _et_ _al_. (118, 119) have studied the effect of pressure on the vibration of ionic crystals at long wavelengths. They find that internal modes of vibration of polyatomic ions (e.g., NO_3^-, SO_4^{2-}) are relatively insensitive to pressure -- the change being about 0.0-0.2 cm^{-1}/kbar of applied pressure. On the other hand, large shifts in frequency were observed for external (lattice) modes, e.g., 0.7-1.9 cm^{-1}/kbar. Based on these findings, Edgell, et al. (10), studied the variation with pressure of the vibrational frequency of lithium chloride in tetrahydrofuran solution. They obtained the average value of 1.5 cm^{-1}/kbar of applied pressure and concluded that the vibration is characteristic of a lattice mode in an ionic solid which means that solvent molecules are also involved in the vibration.

In the present study, the non-shifting of the frequency of lithium chloride band upon substitution of the deuterated tetrahydrofuran as well as the high degree of association of lithium chloride in the solvent, as indicated by vapor pressure osmometric measurements (see below) indicate that the possibility of the vibrational frequency at 389 cm^{-1} arising from the dimer vibration can not be ruled out.

The halides of alkali metals, especially the lithium halides, are known to be polymerized in vapor phase, in matrices and in solvents with low polarities. The occurrence of dimer and trimer molecules in addition to the monomers has been well established. For some of the halides (notably the lighter halides) the dimer to monomer ratio is as high as 3:1 (120-123). The infrared spectra of the lithium salts, both in gaseous phase (124, 125) and in matrices of argon, krypton, xenon and nitrogen (126-128) have been investigated and the vibrational frequencies of the monomers and dimers assigned (124,129). The structure of lithium chloride has also been investigated by electron diffraction (130), which confirmed the theoretical predicted configuration of a planar diamond shaped structure.

There are three vibrational frequencies of the dimers, and with the exception of those of lithium fluoride (which occur at higher frequencies), all the frequencies lie within the 500 to 150 cm^{-1} spectral range. The frequencies are found to be matrix dependent, e.g., in nitrogen matrix, at 20°K, the two higher dimer vibrational frequencies of lithium chloride are at 425 cm^{-1} (b_{3u}) and 325 cm^{-1} (b_{2u}). The presence of lithium bromide tetramers in ether has also been reported (131).

In the light of the findings described above, and from the data obtained in the present study, it is not unreasonable to ascribe the 389 cm^{-1} lithium chloride band in tetrahydrofuran solution to that of the dimer vibration, while the vibrations of lithium iodide and other lithium salts with polyatomic anions may involve the solvent molecules and the anions. Lithium bromide may represent the intermediate case. The dimer vibration is that of the lattice mode, and hence is sensitive to pressure, as was found by Edgell, et al. (10).

Vapor Pressure Osmometric Measurements

The apparent molecular weights of seven lithium and four sodium salts in tetrahydrofuran solutions were measured. The procedure used is the same as that described in the vapor pressure osmometric measurements in acetone solutions. The data obtained are given in Tables 13 and 14. The $\Delta R/C$ vs. C_m calibration curve for the solvent is given in Figure 19. The $\Delta R/C$ vs. C plots for the various salts are given in Figures 20 to 23. A summary of the results obtained is given in Table 15.

From the apparent molecular weights obtained it is seen that none of the salts studied show any degree of dissociation in tetrahydrofuran solutions. Association is appreciable for all the salts, especially at higher concentrations.

Among the salts studied lithium chloride showed the greatest extent of association. In fact, the apparent molecular weight of lithium chloride approaches that of a dimer. The infrared band frequencies of alkali metal salts in tetrahydrofuran solutions are all anion dependent, which indicates that the anions are either still bound to the cations or are present in the near neighbor environment, and together with the solvent molecules, form a cage in which the cations vibrate. Lithium chloride may represent a possible exception in that in view of the strong association of the salt, the solvent, with its low polarity, is unable to break the bond of the dimers. Thus the vibrational band may be due to the dimers, and not the ion pair vibration or vibrations involving solvent molecules.

From the apparent molecular weight at each salt concentration vs. concentration plots, as shown in Figures 24 to 26, it is seen that the apparent molecular weights of all the salts are concentration dependent, though the degree of dependence varies. There is very small concentration dependence of the apparent molecular weights of the lithium and sodium tetraphenylborate salts in acetone solutions. However, in tetrahydrofuran solutions, the apparent molecular weights of the two salts are highly concentration dependent. The contrasting data may reflect the difference in the dissociating powers of the two solvents.

Table 13. Vapor Phase Osmometry Calibration Data - Benzil in Tetrahydrofuran

Run	Conc (M)	ΔR	$\Delta R/C_m$
I	0.1776	72.12	406.0
	0.1110	46.47	418.5
	0.07772	32.65	420.1
	0.05551	23.31	419.9
	0.02924	13.02	445.3
II	0.2018	82.55	409.1
	0.1816	75.02	413.1
	0.1413	57.87	409.7
	0.1211	50.41	416.4
	0.1009	41.96	415.9
	0.07305	31.00	424.4
	0.05549	23.63	425.8
	0.04036	17.34	429.6
	0.03027	13.04	430.8
	0.01514	6.81	449.8
III	0.1989	81.31	408.8
	0.1889	76.88	406.9
	0.1790	73.23	409.1
	0.1691	69.03	408.3
	0.1492	61.36	411.2
	0.1293	53.36	412.8
	0.1094	45.53	416.3
	0.09447	39.28	415.8
	0.07955	33.12	416.3
	0.06464	27.17	420.3
	0.04972	21.10	424.4
	0.03480	15.00	431.0
	0.01989	8.90	447.5

Table 14. Data of Vapor Phase Osmometric Measurements - Biphenyl, Lithium and Sodium Salts

Run	Conc (M)	Conc (g/l)	ΔR	$\Delta R/C_{g/l}$	M_{app}
			Biphenyl		
I	0.1836	28.321	74.90	2.645	154.1
	0.1561	24.072	62.22	2.585	159.0
	0.1280	19.739	51.14	2.591	159.8
	0.09902	15.270	39.70	2.600	160.6
	0.07346	11.328	30.15	2.662	157.8
	0.05510	8.497	22.89	2.694	156.8
	0.03673	5.664	15.37	2.714	156.2
	0.01836	2.832	7.81	2.758	154.5
			$LiNO_3$		
I	0.1532	10.560	36.45	3.452	121.2
	0.1379	9.504	32.92	3.464	121.1
	0.1148	7.917	28.82	3.640	115.5
	0.09957	6.864	25.34	3.692	114.2
	0.08425	5.805	22.12	3.809	110.9
	0.06893	4.752	19.08	4.015	105.5
	0.05361	3.696	15.31	4.142	102.5
	0.03830	2.640	11.69	4.428	96.1
	0.02298	1.584	7.72	4.874	87.5
II	0.1545	10.650	36.80	3.455	121.1
	0.1390	9.585	33.35	3.479	120.5
	0.1236	8.520	30.47	3.576	117.4
	0.1081	7.455	27.50	3.689	114.1
	0.09269	6.390	24.43	3.823	110.4
	0.07724	5.325	21.05	3.953	107.0
	0.06179	4.260	17.56	4.122	102.8
	0.04634	3.195	14.00	4.382	97.0
	0.03090	2.130	10.12	4.751	89.6
	0.01545	1.065	5.72	5.371	79.5

Table 14. (Continued)

Run	Conc (M)	Conc (g/l)	ΔR	$\Delta R/C_{g/l}$	M_{app}
			LiSCN		
I	0.1489	9.682	49.32	5.094	81.4
	0.1314	8.542	44.10	5.163	80.6
	0.1051	6.834	36.40	5.326	78.6
	0.08759	5.695	31.40	5.514	76.2
	0.07007	4.556	25.68	5.637	74.8
	0.05255	3.417	20.20	5.912	71.6
	0.03504	2.278	13.67	6.001	70.8
	0.01752	1.139	7.20	6.321	67.6
II	0.1572	10.220	51.45	5.034	82.2
	0.1415	9.201	46.56	5.060	82.1
	0.1179	7.667	39.94	5.209	80.2
	0.09434	6.134	33.43	5.450	76.9
	0.06289	4.089	23.36	5.713	73.9
	0.04717	3.067	17.92	5.843	72.6
	0.03145	2.045	12.51	6.117	69.5
			$LiClO_4$		
I	0.1381	14.688	46.42	3.160	131.5
	0.1251	13.306	42.30	3.179	131.1
	0.1056	11.233	37.37	3.327	125.7
	0.08121	8.640	29.82	3.451	121.8
	0.06496	6.912	24.87	3.598	117.3
	0.03248	3.456	12.95	3.747	113.4
	0.01624	1.728	6.76	3.912	109.2
II	0.1570	16.700	53.31	3.192	129.7
	0.1334	14.196	45.98	3.239	128.4
	0.1177	12.525	41.62	3.323	125.5
	0.09418	10.021	34.49	3.442	121.7
	0.07848	8.350	29.56	3.540	118.8
	0.06671	7.098	25.78	3.632	116.1
	0.05494	5.846	21.65	3.703	114.2
	0.03924	4.175	15.68	3.756	113.0
	0.02747	2.923	11.27	3.856	110.4

Table 14. (Continued)

Run	Conc (M)	Conc (g/l)	ΔR	$\Delta R/C_{g/l}$	M_{app}
LiCl					
I	0.1613	6.840	32.74	4.787	87.6
	0.1372	5.814	27.68	4.761	88.4
	0.1210	5.130	25.00	4.873	86.6
	0.1049	4.446	21.71	4.883	86.6
	0.08068	3.420	17.28	5.053	83.9
	0.06454	2.736	13.82	5.051	84.1
	0.04841	2.052	10.83	5.278	80.7
	0.03631	1.539	8.30	5.393	79.1
	0.02017	0.855	4.90	5.731	74.6
II	0.1503	6.370	30.53	4.793	87.6
	0.1277	5.415	26.16	4.831	87.2
	0.1127	4.777	23.39	4.896	86.2
	0.08265	3.503	17.68	5.047	84.0
	0.07514	3.185	16.25	5.102	83.1
	0.06011	2.548	13.22	5.188	81.9
	0.04508	1.911	10.21	5.343	79.7
	0.03005	1.274	7.12	5.589	76.4
LiBr					
I	0.1534	13.320	41.85	3.142	132.7
	0.1304	11.322	35.73	3.156	132.7
	0.1150	9.990	32.20	3.223	130.2
	0.09969	8.658	28.74	3.320	126.8
	0.07669	6.661	23.13	3.473	121.5
	0.06135	5.328	18.71	3.512	120.6
	0.04601	3.996	14.49	3.626	117.1
	0.03451	2.997	11.51	3.831	110.8
	0.01917	1.665	6.91	4.150	102.9
II	0.1506	13.080	41.16	3.147	132.5
	0.1355	11.772	37.56	3.191	131.0
	0.1054	9.156	30.29	3.308	127.0
	0.09036	7.848	26.07	3.322	126.9
	0.07154	6.213	21.72	3.496	120.9
	0.05648	4.905	17.94	3.658	115.9
	0.04142	3.597	13.61	3.784	112.3
	0.03012	2.616	11.16	4.266	99.0

Table 14. (Continued)

Run	Conc(M)	Conc (g/l)	ΔR	$\Delta R/C_{g/1}$	M_{app}
		<u>LiI</u>			
I	0.1640	21.950	51.27	2.336	177.2
	0.1476	19.755	47.05	2.382	174.5
	0.1312	17.560	43.20	2.460	169.3
	0.1148	15.366	37.81	2.461	169.9
	0.09839	13.171	32.86	2.495	168.1
	0.08199	10.975	28.32	2.580	163.1
	0.06559	8.780	23.14	2.636	160.1
	0.04919	6.585	17.97	2.729	155.4
	0.03280	4.391	12.31	2.804	151.8
	0.01640	2.195	6.36	2.898	147.3
II	0.1559	20.860	49.50	2.373	174.8
	0.1403	18.777	44.40	2.365	175.9
	0.1247	16.690	41.73	2.500	166.8
	0.1013	13.560	34.65	2.555	164.0
	0.07793	10.432	27.30	2.617	160.9
	0.06234	8.345	22.97	2.753	153.4
	0.04675	6.259	17.57	2.807	151.0
	0.03896	5.215	14.78	2.834	149.9
	0.02727	3.650	10.90	2.986	142.6
		<u>$LiBPh_4$</u>			
I	0.1025	33.448	31.41	0.939	447.2
	0.08716	28.432	26.61	0.936	450.0
	0.07178	23.415	22.45	0.959	440.6
	0.06152	20.068	19.63	0.978	432.6
	0.05127	16.724	16.76	1.002	423.1
	0.04102	13.381	14.06	1.051	404.5
	0.03076	10.034	11.06	1.102	386.2
	0.02051	6.690	7.82	1.168	365.2
	0.01025	3.344	4.46	1.334	320.6
II	0.09660	31.510	30.50	0.970	434.1
	0.08211	26.785	26.22	0.979	430.6
	0.07245	23.634	23.54	0.996	423.7
	0.05796	18.907	19.43	1.028	411.9
	0.04589	14.968	16.27	1.087	390.2
	0.03623	11.818	13.22	1.119	379.9
	0.02657	8.666	10.05	1.160	367.4
	0.01691	5.516	6.93	1.256	339.9

Table 14. (Continued)

Run	Conc (M)	Conc (g/l)	ΔR	$\Delta R/C_{g/l}$	M_{app}
			$NaBPh_4$		
I	0.1031	35.251	34.06	0.966	433.6
	0.08836	30.240	30.00	0.992	423.8
	0.07363	25.199	24.86	0.987	427.8
	0.05890	20.158	20.22	1.003	421.8
	0.04418	15.120	16.18	1.070	396.5
	0.02945	10.079	11.45	1.136	374.8
	0.01473	5.040	6.25	1.240	344.3
II	0.1130	38.680	36.40	0.941	444.7
	0.09183	31.428	30.25	0.963	436.6
	0.07064	24.176	23.80	0.984	428.7
	0.05298	18.132	18.55	1.023	414.0
	0.03885	13.296	14.30	1.076	395.0
	0.02119	7.251	8.71	1.201	355.1
			$NaClO_4$		
I	0.1402	17.172	39.97	2.328	179.4
	0.1169	14.310	34.88	2.437	171.2
	0.09349	11.448	28.89	2.524	166.6
	0.06233	7.632	20.38	2.670	160.7
	0.04675	5.725	16.21	2.831	158.4
	0.03116	3.816	11.55	3.027	149.9
	0.01558	1.908	6.29	3.297	140.6
II	0.1538	18.830	42.90	2.278	182.9
	0.1307	16.005	37.50	2.343	178.4
	0.1077	13.182	31.91	2.421	173.5
	0.08458	10.357	26.41	2.550	165.2
	0.06920	8.474	22.40	2.643	159.8
	0.05382	6.590	17.93	2.721	155.8
	0.03845	4.708	13.47	2.861	148.6
	0.02307	2.825	8.97	3.175	134.2

Table 14. (Continued)

Run	Conc (M)	Conc (g/l)	ΔR	$\Delta R/C_{g/l}$	M_{app}
			NaI		
I	0.1535	23.010	42.00	1.825	228.3
	0.1264	18.948	35.85	1.892	221.3
	0.1083	16.242	31.71	1.952	215.1
	0.09028	13.535	26.82	1.982	212.4
	0.07222	10.827	22.14	2.045	206.6
	0.05417	8.121	17.46	2.150	197.2
	0.03611	5.414	12.26	2.265	187.8
	0.01806	2.707	6.87	2.538	168.2
II	0.1638	24.560	44.52	1.813	229.5
	0.1393	20.876	38.43	1.841	227.1
	0.1147	17.191	32.75	1.905	220.2
	0.09830	14.737	28.82	1.956	215.1
	0.08192	12.281	24.34	1.982	212.9
	0.06554	9.826	20.32	2.068	204.5
	0.04915	7.369	16.25	2.205	192.4
	0.02458	3.685	8.74	2.372	179.8
			NaSCN		
I	0.1682	13.640	41.96	3.076	135.6
	0.1262	10.230	32.20	3.148	133.4
	0.1009	8.184	26.29	3.212	131.2
	0.08412	6.820	22.55	3.306	127.7
	0.06729	5.456	18.77	3.440	123.1
	0.05047	4.092	14.68	3.587	118.4
	0.03365	2.728	10.64	3.900	109.2
	0.01682	1.364	5.73	4.201	101.7
II	0.1639	13.290	40.37	3.038	137.4
	0.1475	11.961	36.16	3.023	138.4
	0.1311	10.632	33.14	3.117	134.5
	0.1147	9.303	29.23	3.142	133.8
	0.09015	7.309	23.86	3.265	129.3
	0.07376	5.981	19.90	3.327	127.1
	0.05737	4.652	16.06	3.452	122.9
	0.04098	3.323	12.31	3.705	114.8
	0.02459	1.994	7.95	3.987	107.0

Table 15. The Apparent Molecular Weights of Alkali Metal Salts in Tetrahydrofuran

Calibration Constant K_m = 429

Salt	$(\Delta R/C_{g/1})_{C=0}$	Mol. Wt. (apparent)	Mol. Wt. (real)	$\frac{M_{app}}{M_{real}}$	Linear Conc. Range (M)*
LiCl	5.54	77.4	42.4	1.83	0.04 - 0.14
LiBr	4.03	106.5	86.9	1.23	0.03 - 0.13
LiI	2.96	144.9	133.8	1.08	0.02 - 0.16
$LiNO_3$	4.59	93.5	68.9	1.36	0.05 - 0.14
LiSCN	6.18	69.4	65.0	1.07	0.02 - 0.14
$LiClO_4$	4.01	107.0	106.4	1.01	0.02 - 0.14
$LiBPh_4$	1.27	337.8	326.2	1.04	0.02 - 0.09
NaI	2.30	186.5	149.9	1.24	0.03 - 0.16
NaSCN	3.74	114.7	81.1	1.41	0.05 - 0.15
$NaClO_4$	3.00	143.0	122.4	1.17	0.04 - 0.15
$NaBPh_4$	1.14	376.3	342.2	1.10	0.02 - 0.11
Biphenyl	2.75	156.0	154.2	1.01	0.02 - 0.16

*In the $\Delta R/C_{g/1}$ _vs_. C plots.

Figure 19. The $\Delta R/C_m$ *vs*. C_m calibration plot. Benzil in tetrahydrofuran.

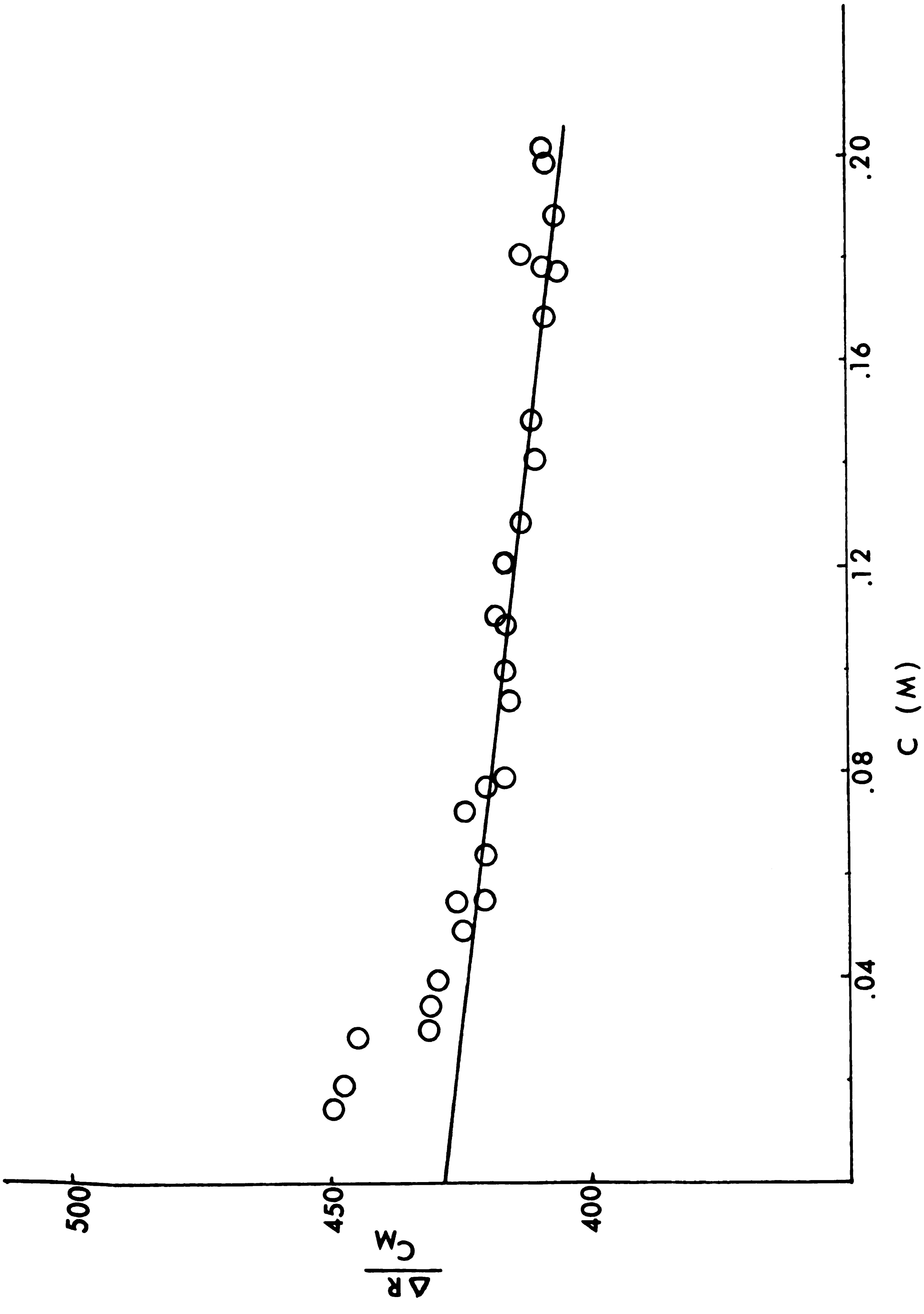

Figure 19.

Figure 20. The $\Delta R/C_{g/l}$ vs. $C_{g/l}$ plots. A. LiCl. B. LiSCN. C. $LiNO_3$.

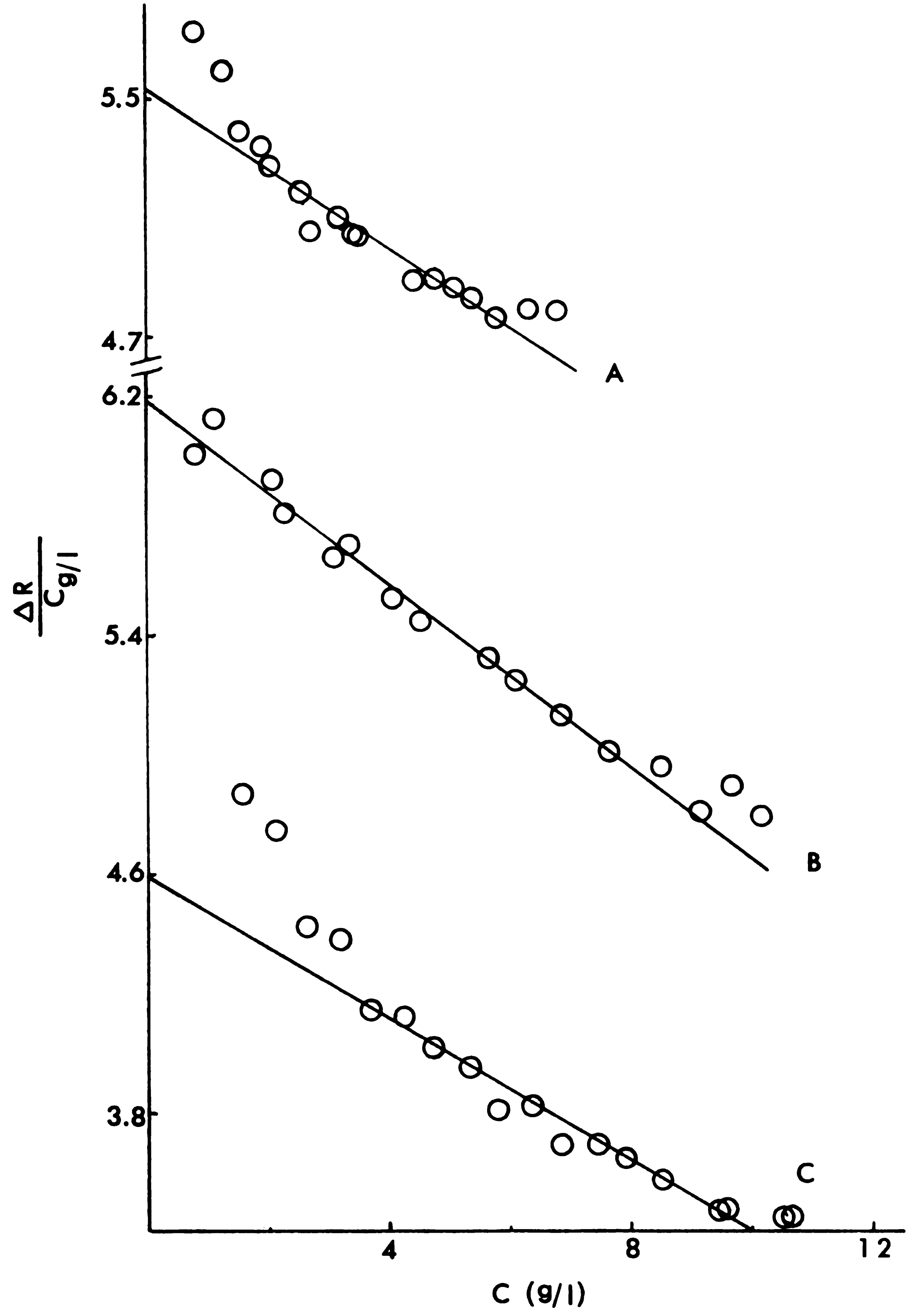

Figure 20.

Figure 21. The $\Delta R/C_{g/l}$ vs. $C_{g/l}$ plots. A. NaSCN. B. LiBr. C. $LiClO_4$.

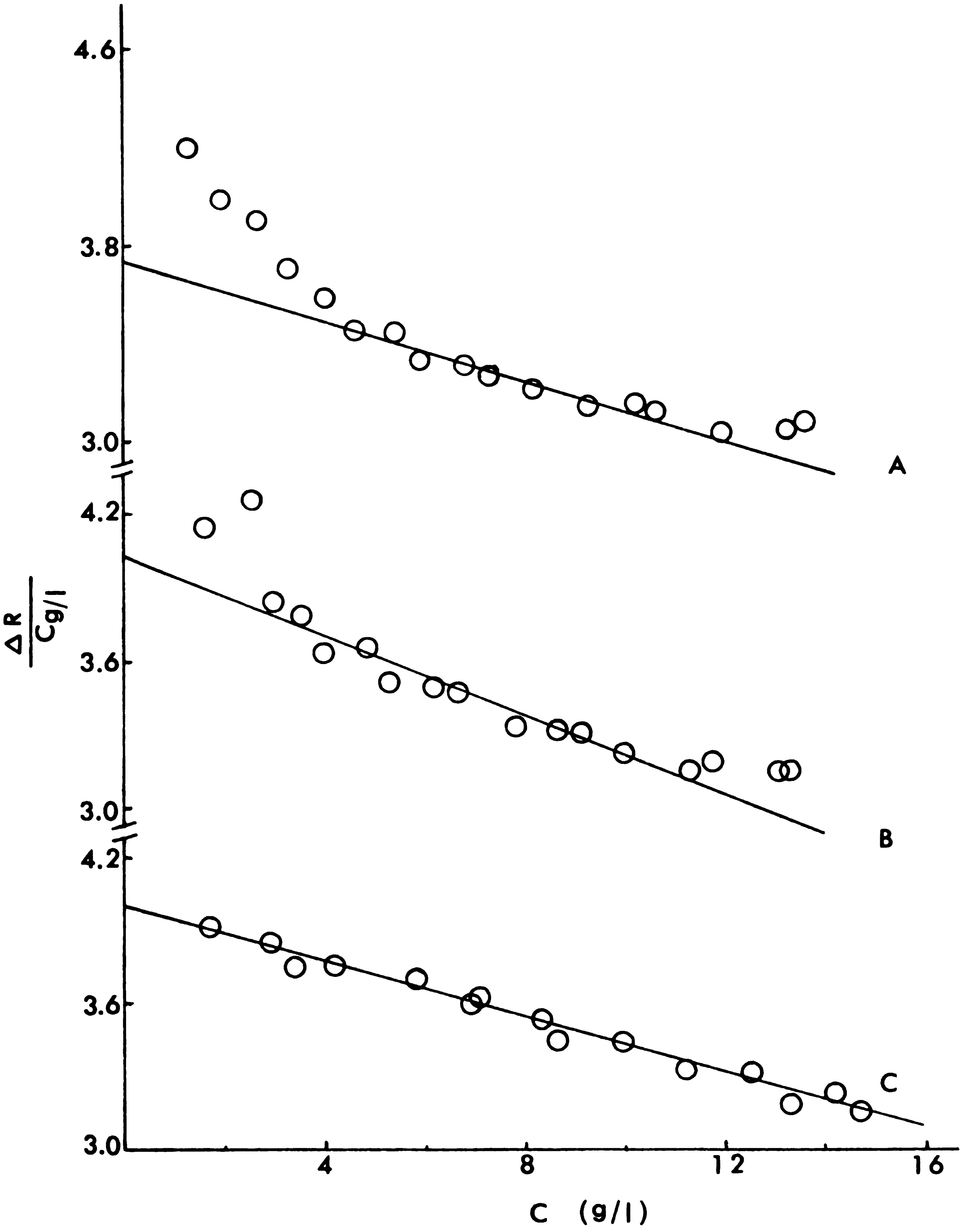

Figure 21.

Figure 22. The $\Delta R/C_{g/l}$ vs. $C_{g/l}$ plots. A. Biphenyl. B. $NaBPh_4$. C. $LiBPh_4$.

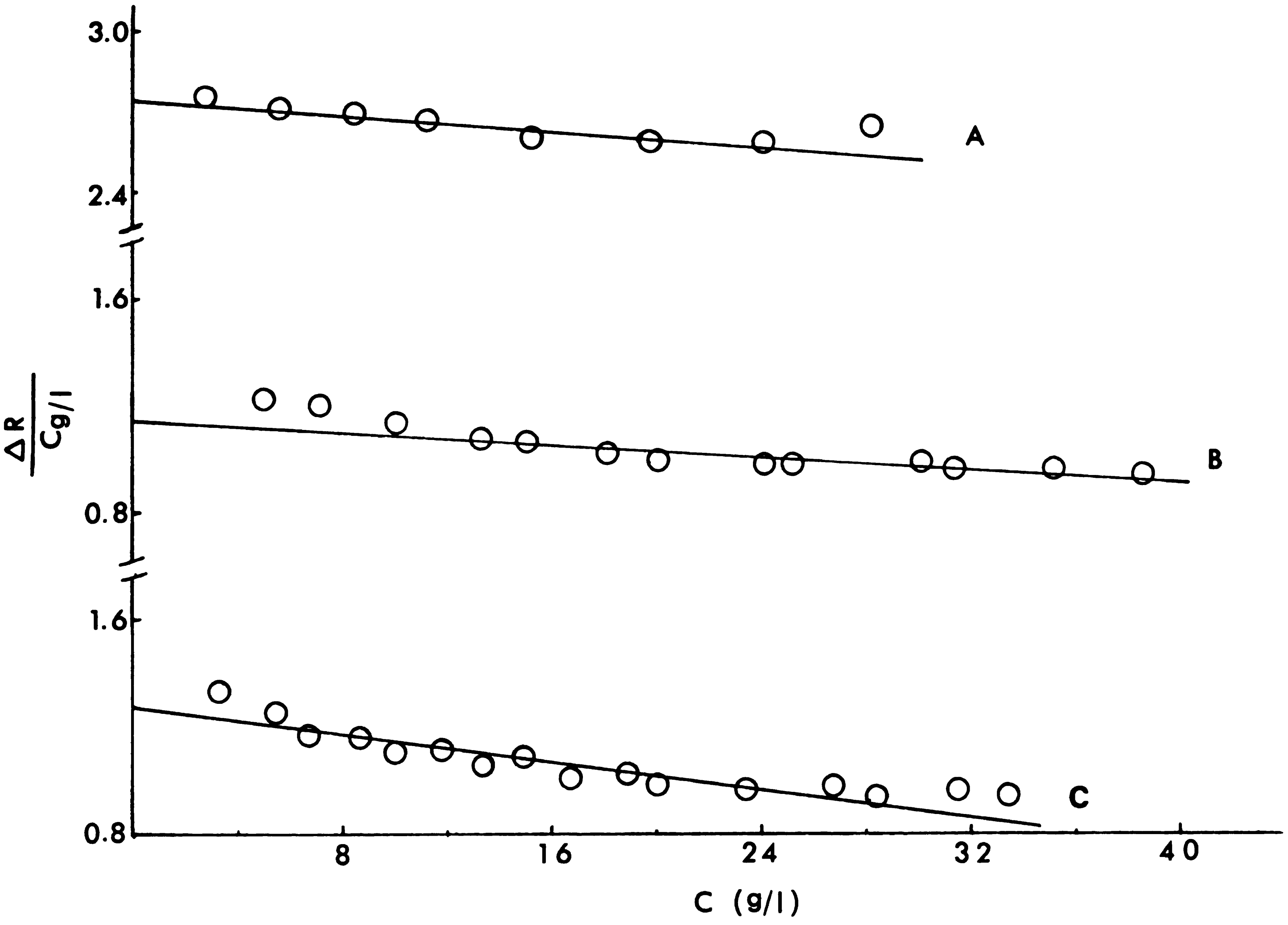

Figure 22.

Figure 23. The $\Delta R/C_{g/l}$ vs. $C_{g/l}$ plots. A. $NaClO_4$. B. LiI. C. NaI.

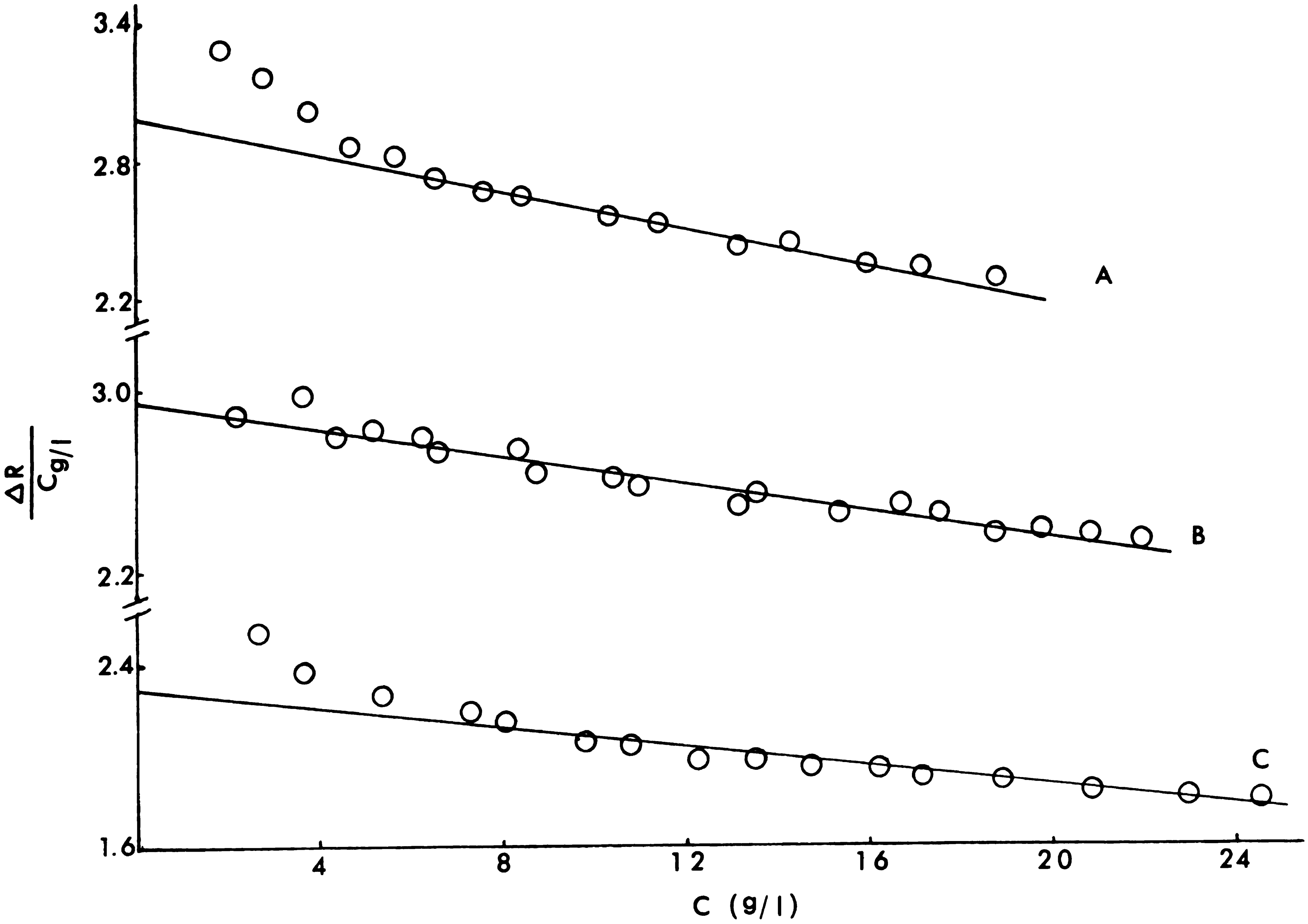

Figure 23.

Figure 24. The apparent molecular weights (M_{app}) *vs.* molar concentration plots. A. $LiBPh_4$. B. $LiClO_4$. C. $LiNO_3$. D. LiSCN.

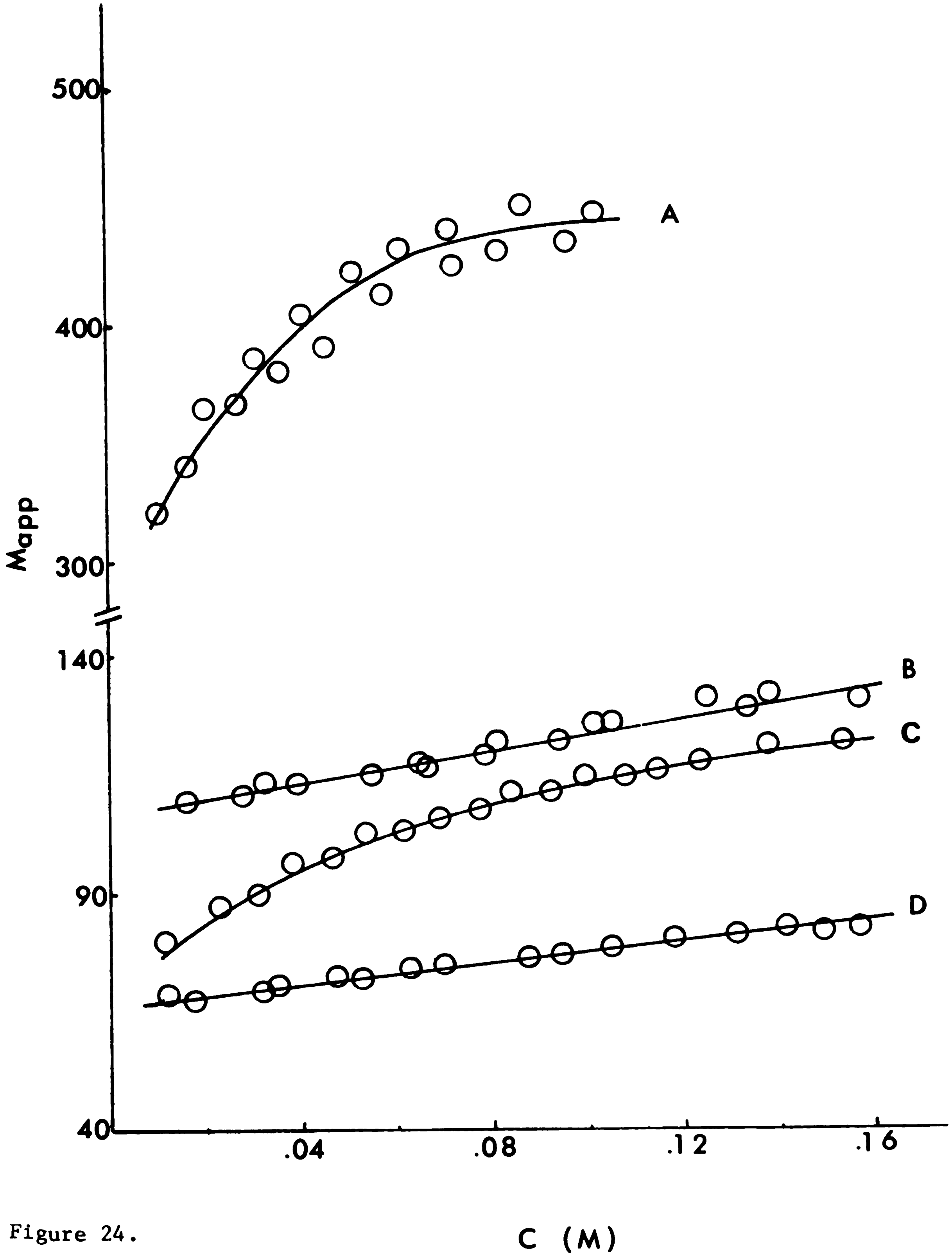

Figure 24.

Figure 25. The apparent molecular weights (M_{app}) vs. molar concentration plots. A. Biphenyl. B. LiI. C. LiBr. D. LiCl.

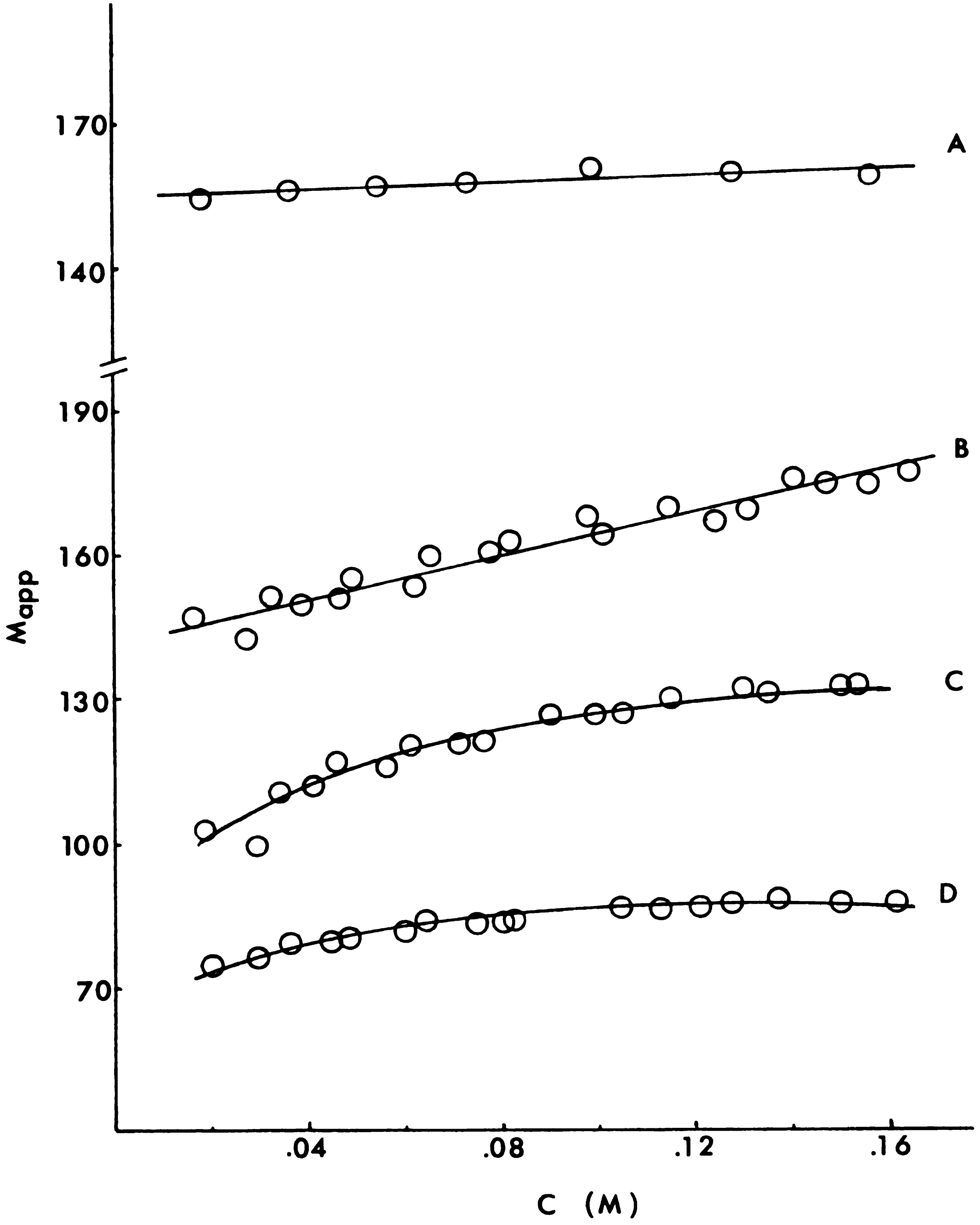

Figure 25.

Figure 26. The apparent molecular weights vs. molar concentration plots. A. $NaBPh_4$. B. NaI. C. $NaClO_4$. D. NaSCN.

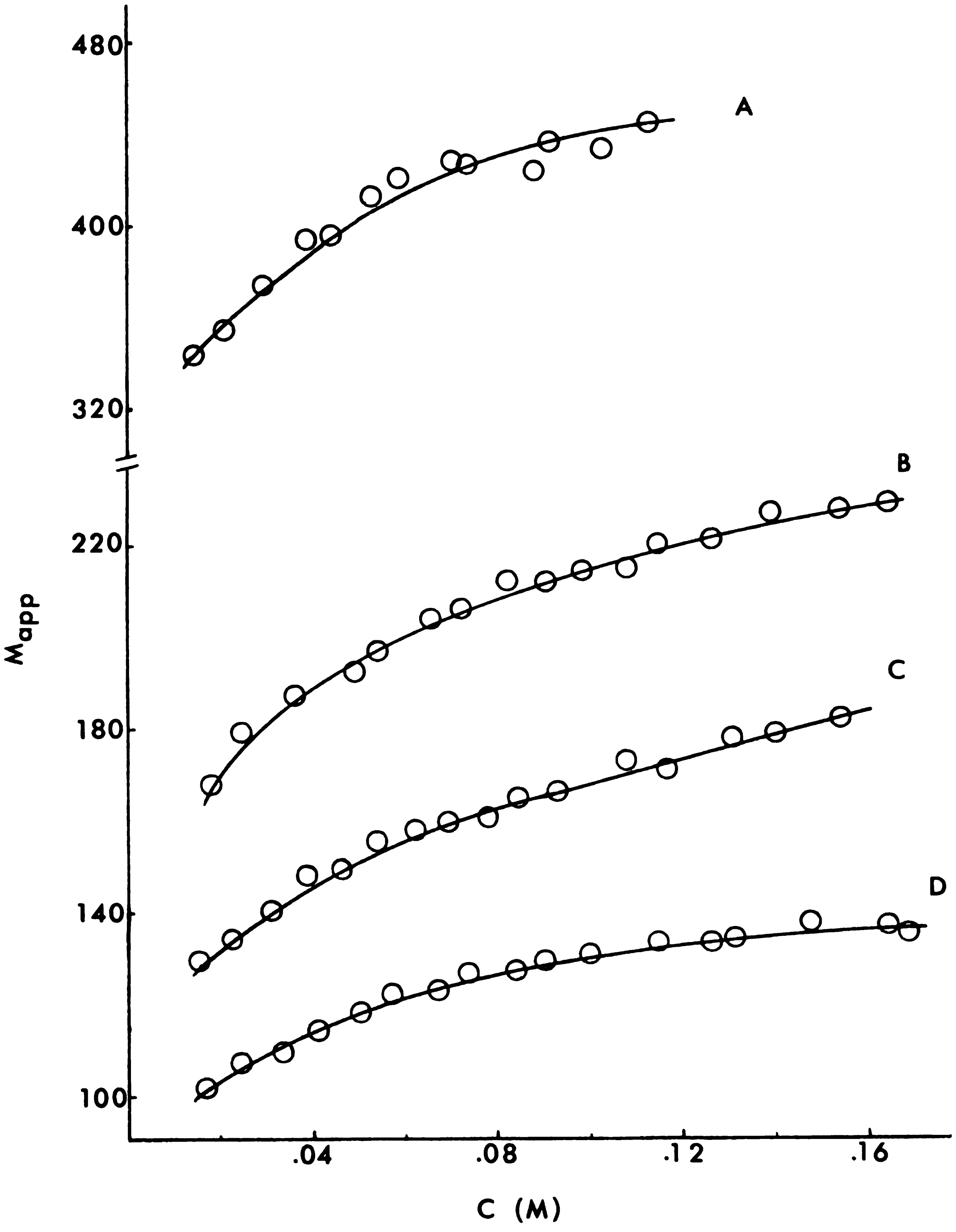

Figure 26.

(E) Mixed Solvents

In these studies, six mixed solvent systems have been examined by proton magnetic resonance technique. The standard salt was lithium perchlorate which was used in all the systems, while tetrabutylammonium perchlorate and tetrabutylammonium bromide were used in some of the systems.

The six mixed solvent systems are listed below (they will be designated as solvent I, solvent II, etc. in subsequent discussions):

(I) 2.0 M acetone in acetic acid (14.8 M).
(II) 2.0 M acetic acid in acetone (12.0 M).
(III) 2.0 M dimethyl sulfoxide (DMSO) in acetone (11.7 M).
(IV) 2.0 M acetone in dimethyl sulfoxide (12.0 M).
(V) 2.0 M dimethyl sulfoxide in acetic acid (15.0 M).
(VI) 1.2 M dimethyl sulfoxide and 1.2 M acetone in nitromethane (15.3 M).

Results are discussed separately below.

Solvent I. 2.0 M Acetone in Acetic Acid

The effects of lithium perchlorate, tetrabutylammonium perchlorate and tetrabutylammonium bromide, at various concentrations, on the proton chemical shifts of acetone and acetic acid were examined. The data obtained are given in Table 16. The mole ratio plots for lithium perchlorate are shown in Figure 27.

From the data, it is seen that when chemical shifts are plotted vs. the mole ratio of acetone/$LiClO_4$, smooth curves are obtained for both acetone and acetic acid. The hydroxyl proton of acetic acid has the largest shifts in the concentration range studied. The large shift is probably due to the breaking up of the hydrogen-bonds of acetic acid by the addition of salts.

Solvent II. 2.0 M Acetic Acid in Acetone

Studies similar to that for Solvent I were carried out for solvent mixtures II - 2.0 M acetic acid in acetone. The data obtained are listed in Table 17. The mole ratio plots are shown in Figure 28.

Again smooth curves were obtained when chemical shifts were plotted vs. mole ratio of acetic acid/$LiClO_4$. From the comparison of the two solvent systems (I and II), it is apparent that the chemical shift of the hydroxyl proton of acetic acid is strongly concentration dependent (from 685 Hz in Solvent I to 622 Hz in Solvent II). Thus in Solvent I, where acetic acid is the major component, the hydroxyl proton resonance is shifted upfield (685 to 624 Hz) with addition of lithium perchlorate (and a very small shift for tetrabutylammonium salts), indicating a decrease in hydrogen-bonding. However, in Solvent II, the opposite trend is observed upon the addition of lithium perchlorate and tetrabutylammonium bromide, although to a smaller degree. The shifting of the hydroxyl proton resonance indicates an increase in hydrogen-bonding upon the addition of salts. Since the lithium ion is appreciably solvated by acetone, an increase in the salt concentration will decrease the concentration of free acetone. Consequently acetone - acetic acid interaction will likewise decrease, resulting in greater hydrogen-bonding interaction between acetic acid molecules. In the case of the tetrabutylammonium bromide, the presence of the bromide anion may enhance hydrogen-bonding due to the interaction between the bromide anion and the hydroxyl proton of acetic acid. However, the shifting is small (maximum about 12 Hz) and at high salt concentration the hydroxyl resonance peak became appreciably broad and weak. The addition of tetrabutylammonium perchlorate caused negligible shifting of the resonance peaks of the acetone protons and the methyl protons of acetic acid. However, the hydroxyl proton of acetic acid is shifted slightly upfield, opposite to that observed for lithium perchlorate and tetrabutylammonium bromide. This gives additional evidence (see acetone section) that tetrabutylammonium perchlorate does not interact with acetone and acetic acid.

Solvent III. 2.0 M Dimethyl Sulfoxide in Acetone

The effects of three salts, lithium perchlorate, tetrabutylammonium perchlorate and tetrabutylammonium bromide on the proton chemical shifts of dimethyl sulfoxide and acetone in Solvent III were measured. The data obtained are given in Table 18. The mole ratio plots are shown in Figure 29. Though acetone molecules are present in excess in this solvent system, the resonance peak of the dimethyl sulfoxide protons still shifted with the addition of lithium perchlorate, indicating preferential solvation of the lithium ions by dimethyl sulfoxide molecules. The shifting of the acetone proton resonance peak becomes appreciable only at high salt concentration. Again the addition of tetrabutylammonium salts caused relatively very small shiftings of the proton resonance peaks of the two solvent components.

Solvent IV. 2.0 M Acetone in Dimethyl Sulfoxide

Studies similar to that of Solvents I, II, and III were performed in Solvent IV, which is 2.0 M acetone in dimethyl sulfoxide. The data obtained are given in Table 19. The mole ratio plots are shown in Figure 30.

From the data obtained from solvents I, II, III and IV, it is evident that dimethyl sulfoxide is a stronger donor than acetone and acetic acid. Thus, even with excess acetone, dimethyl sulfoxide molecules can still compete successfully for the lithium ion. This can be seen from the large chemical shifts of dimethyl sulfoxide protons and relatively very small shifts for the acetone protons at DMSO/$LiClO_4$ ratio above 2:1. The same is not observed in Solvents I and II, mixed solvent systems of acetone and acetic acid. Thus it is reasonable to assume that the difference between donor strength of acetone and acetic acid probably is small. That this is the case can be seen from Figures 27 and 28. Smooth curves were obtained for both acetone and acetic acid in Solvents I and II, showing that both can compete well for the lithium ion (and possibly anion).

Solvent V. 2.0 M Dimethyl Sulfoxide in Acetic Acid

In Solvent V, which is 2.0 M dimethyl sulfoxide in acetic acid, the proton resonance peak of dimethyl sulfoxide was shifted appreciably downfield, indicating some interaction between the two components in the solvent system. Dimethyl sulfoxide is well known for its weak basicity and thus its ability to accept a proton from an acid (132). Hence it is likely that the dimethyl sulfoxide interacts with the hydroxyl proton of the acetic acid, causing a downfield shift of the dimethyl sulfoxide proton resonance peak. Due to this interaction, relatively small shifts for the dimethyl sulfoxide proton resonance peak were observed upon the addition of lithium perchlorate. The chemical shift of the hydroxyl proton of acetic acid is similar to that observed in

Solvent I - as hydrogen-bonds were broken up, an upfield shift resulted for the hydroxyl proton resonance peak. The data obtained are given in Table 20. The mole ratio plots are shown in Figure 31.

Solvent VI. 1.2 M Dimethyl Sulfoxide and 1.2 M Acetone in Nitromethane

Solvent VI was a three component solvent system consisting of 1.2 M dimethyl sulfoxide and 1.2 M acetone in nitromethane. In this system, as in Solvent III, the resonance peak of the methyl protons of dimethyl sulfoxide has the largest shift upon addition of lithium perchlorate. The acetone peak showed appreciable shift when lithium perchlorate concentration was above 0.3 M. Practically no shifting was observed for the resonance peak of methyl protons of nitromethane at lithium perchlorate concentration below 1.2 M. Above 1.2 M salt concentration, the shifting of the nitromethane peak became noticeable, indicating interaction between the lithium perchlorate and nitromethane molecules.

The data obtained are given in Table 21. The mole ratio plots are shown in Figure 32.

From the data obtained for the six solvent systems, it is evident that dimethyl sulfoxide is the strongest donor solvent, and that the donating abilities of acetone and acetic acid are at about the same level. However, since practically all the curves are smooth, no quantitative relative donor strength of the various component solvents can be ascertained.

Table 16. Chemical Shifts (Hz) of Acetone and Acetic Acid Protons in Solvent I

Salt	Conc (M)	Mole Ratio (Acetone/Salt)	Acetone	Acetic Acid $-CH_3$	Acetic Acid $-COOH$
Blank	--	--	128.9	122.3	688.5
$LiClO_4$	0.216	9.40	130.3	123.2	679.5
	0.257	7.90	130.8	123.5	686.0
	0.276	7.25	130.8	123.7	685.5
	0.299	6.80	130.8	123.5	682.5
	0.347	5.85	131.1	123.7	682.5
	0.405	5.00	131.2	123.8	680.0
	0.461	4.40	131.5	123.9	683.0
	0.531	3.82	131.9	124.2	678.0
	0.628	3.19	132.0	124.5	680.5
	0.815	2.49	132.9	125.0	675.0
	1.00	2.03	133.4	125.3	672.0
	1.28	1.56	133.8	125.9	668.5
	1.51	1.34	134.2	126.3	661.5
	1.84	1.09	135.1	127.2	655.0
	2.55	0.80	136.0	128.2	640.0
	3.1	$\sim$0.65	136.8	129.4	624.0
Bu_4NClO_4	0.103	20	129.6	122.8	688.5
	0.91	$\sim$2	130.1	123.2	675.0
Bu_4NBr	0.131	15	129.4	122.7	681.0
	0.85	$\sim$2	130.1	123.8	674.0

Figure 27. Chemical shifts of the acetone and acetic acid protons vs. Acetone/$LiClO_4$ mole ratio in Solvent I. A. Hydroxyl proton of acetic acid. B. Acetone. C. Methyl protons of acetic acid.

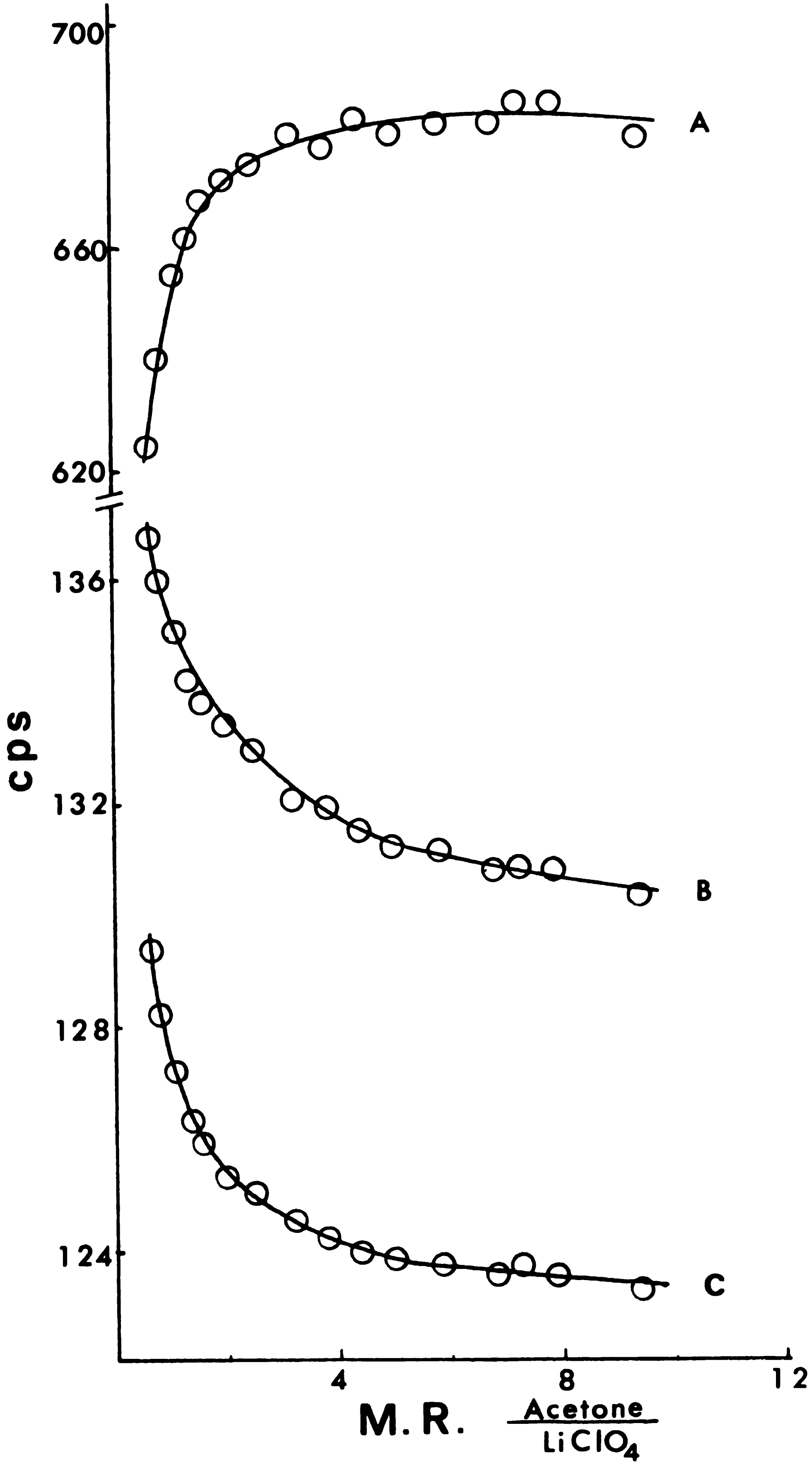

Figure 27.

Table 17. Chemical Shifts (Hz) of Acetone and Acetic Acid Protons in Solvent II

Salt	Conc (M)	Mole Ratio (HOAc/Salt)	Acetone	Acetic Acid $-CH_3$	Acetic Acid -COOH
Blank	--	--	125.3	118.5	622.0
$LiClO_4$	0.201	10.0	126.5	119.3	621.0
	0.244	8.30	126.7	119.4	623.0
	0.285	7.10	127.0	119.8	626.0
	0.342	5.90	127.2	120.0	622.0
	0.406	4.97	127.5	120.3	626.0
	0.487	4.15	127.6	120.4	626.5
	0.567	3.56	128.3	121.0	624.0
	0.686	2.95	128.7	121.4	628.0
	0.808	2.50	128.9	121.8	627.5
	0.903	2.24	129.1	121.9	629.0
	1.07	1.79	129.7	122.5	631.0
	1.38	1.47	130.9	123.7	629.5
	1.70	1.19	131.9	124.5	634.0
	2.81	∿0.7	134.9	127.4	636.0
Bu_4NClO_4	0.119		125.7	118.6	618.5
	0.347		126.2	118.8	615.5
	0.983		126.7	119.3	610.0
Bu_4NBr	0.131		126.1	119.0	620.0
	1.08		127.5	121.5	635.0

Figure 28. Chemical shifts of the acetone and acetic acid protons *vs*. HOAc/$LiClO_4$ mole ratio in Solvent II. A. Hydroxyl proton of acetic acid. B. Acetone. C. Methyl protons of acetic acid.

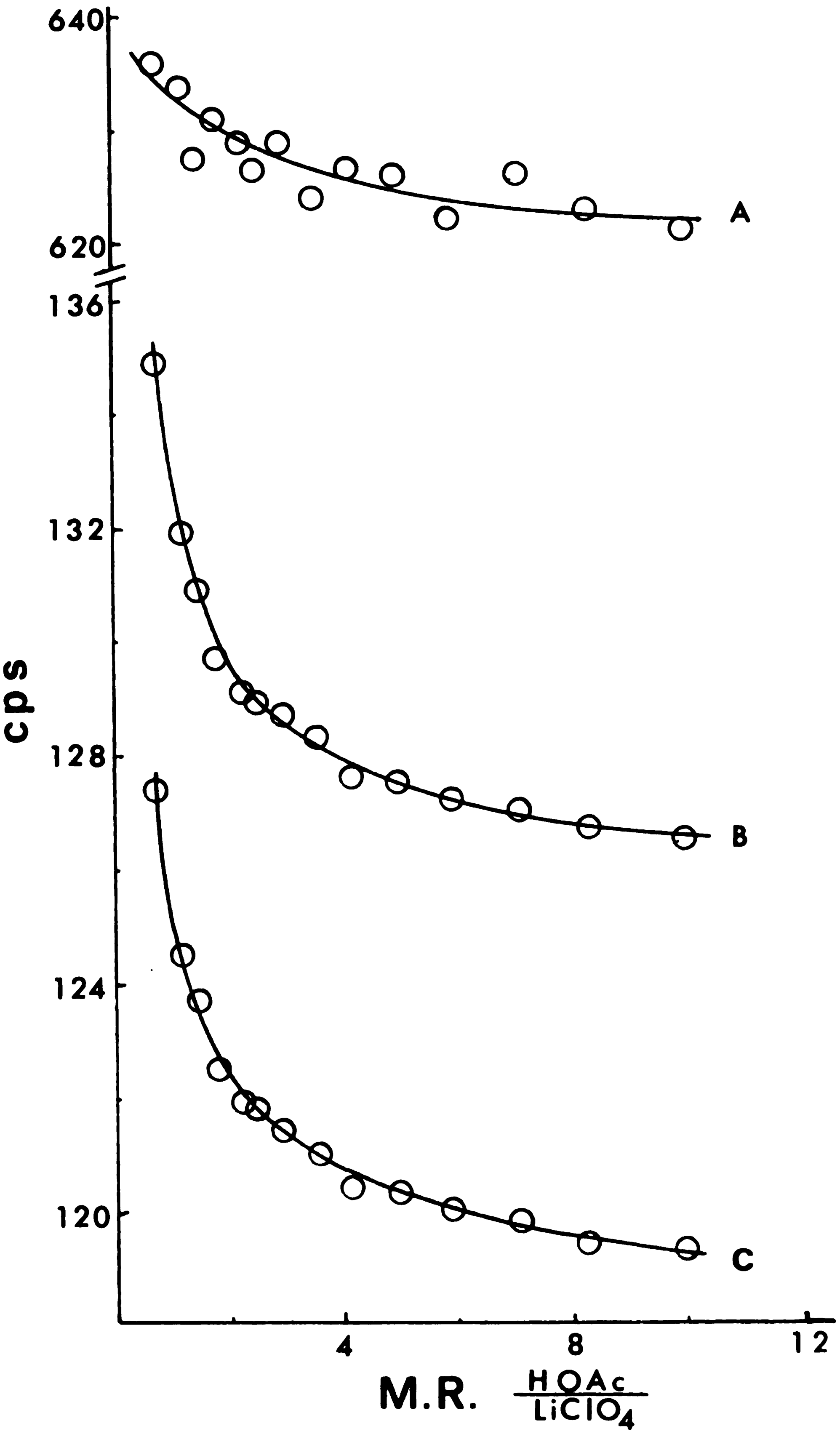

Figure 28.

Table 18. Chemical Shifts (Hz) of Acetone and Dimethyl Sulfoxide Protons in Solvent III

Salt	Conc (M)	Mole Ratio (DMSO/$LiClO_4$)	Acetone	DMSO
Blank	--	--	125.3	151.3
$LiClO_4$	0.149	13.4	125.6	154.5
	0.184	10.9	125.8	155.3
	0.244	8.20	126.1	156.7
	0.282	7.10	126.1	157.4
	0.331	6.05	126.0	158.0
	0.371	5.40	126.1	158.7
	0.414	4.82	126.3	159.4
	0.485	4.13	126.3	160.1
	0.590	3.49	126.7	161.3
	0.087	2.91	126.8	161.7
	0.806	2.48	127.6	162.7
	0.940	2.13	127.3	162.8
	1.23	1.63	129.0	164.0
	1.51	1.33	129.7	164.3
	1.98	1.0	131.6	164.6
	2.69	$\sim$0.7	133.5	165.3
Bu_4NClO_4	0.233	--	124.6	151.2
	0.905	--	125.9	152.7
Bu_4NBr	0.381	--	125.7	154.0
	0.908	--	127.0	157.5

Figure 29. Chemical shifts of the dimethyl sulfoxide and acetone protons *vs*. DMSO/$LiClO_4$ mole ratio in Solvent III. A. DMSO. B. Acetone.

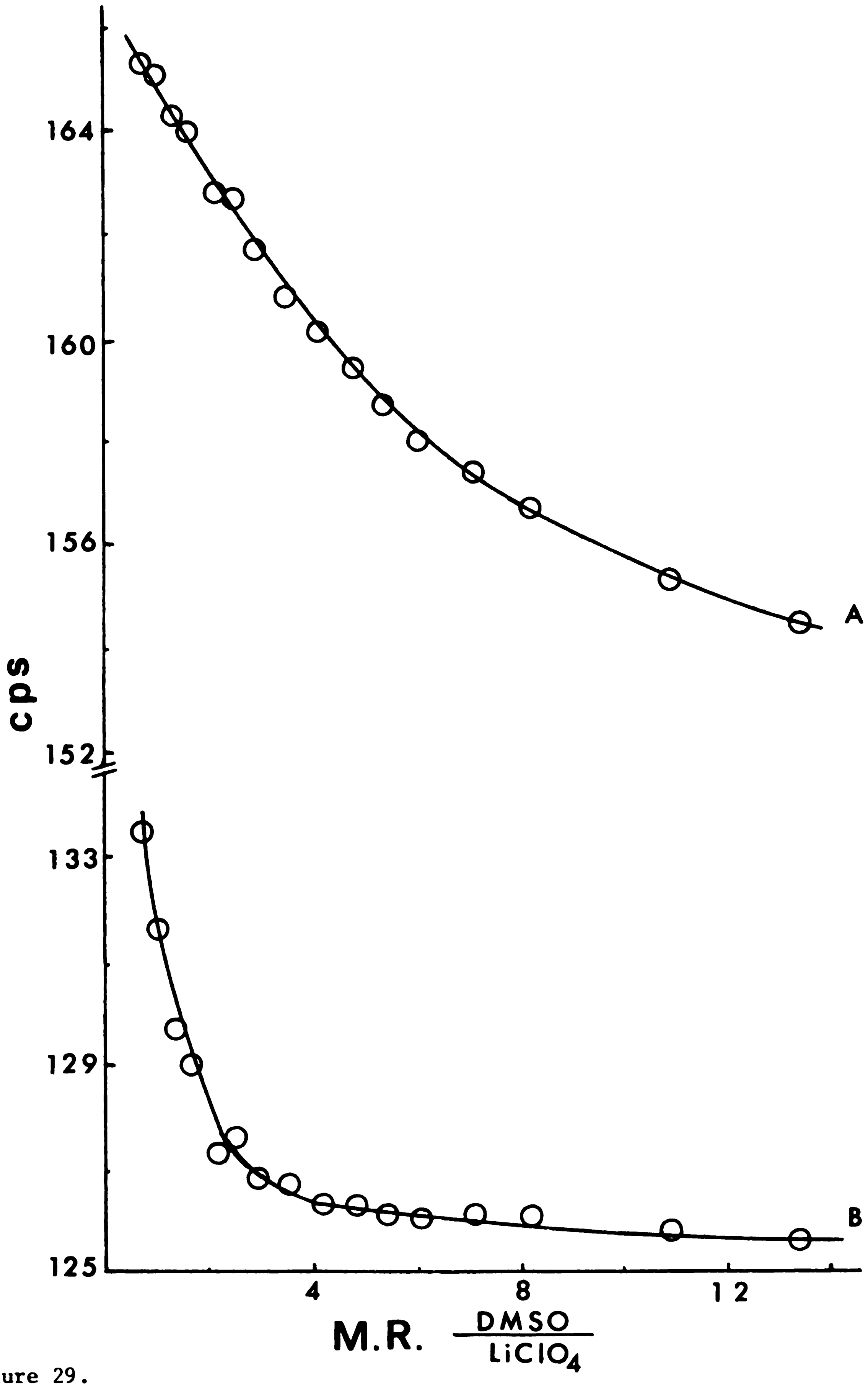

Figure 29.

Table 19. Chemical Shifts (Hz) of Dimethyl Sulfoxide and Acetone Protons in Solvent IV

Salt	Conc (M)	Mole Ratio (Acetone/$LiClO_4$)	DMSO	Acetone
Blank	--	--	151.9	124.7
$LiClO_4$	0.210	9.60	153.2	125.2
	0.239	8.41	152.9	125.0
	0.305	6.60	153.4	125.2
	0.349	5.76	153.5	125.4
	0.396	5.07	153.7	125.4
	0.468	4.28	154.1	125.6
	0.528	3.81	153.8	125.3
	0.595	3.38	154.2	125.2
	0.668	3.01	154.1	125.3
	0.812	2.48	154.9	125.7
	1.06	1.90	155.4	125.6
	1.54	1.31	156.7	126.2
	2.01	1	157.8	126.8
	2.6	0.7	159.1	127.6
Bu_4NClO_4	0.242	--	151.9	124.6
	0.852	--	152.0	124.8
Bu_4NBr	0.199	--	152.7	125.0
	0.924	--	155.4	126.1

Figure 30. Chemical shifts of the dimethyl sulfoxide and acetone protons vs. Acetone/$LiClO_4$ mole ratio in Solvent IV. A. DMSO. B. Acetone.

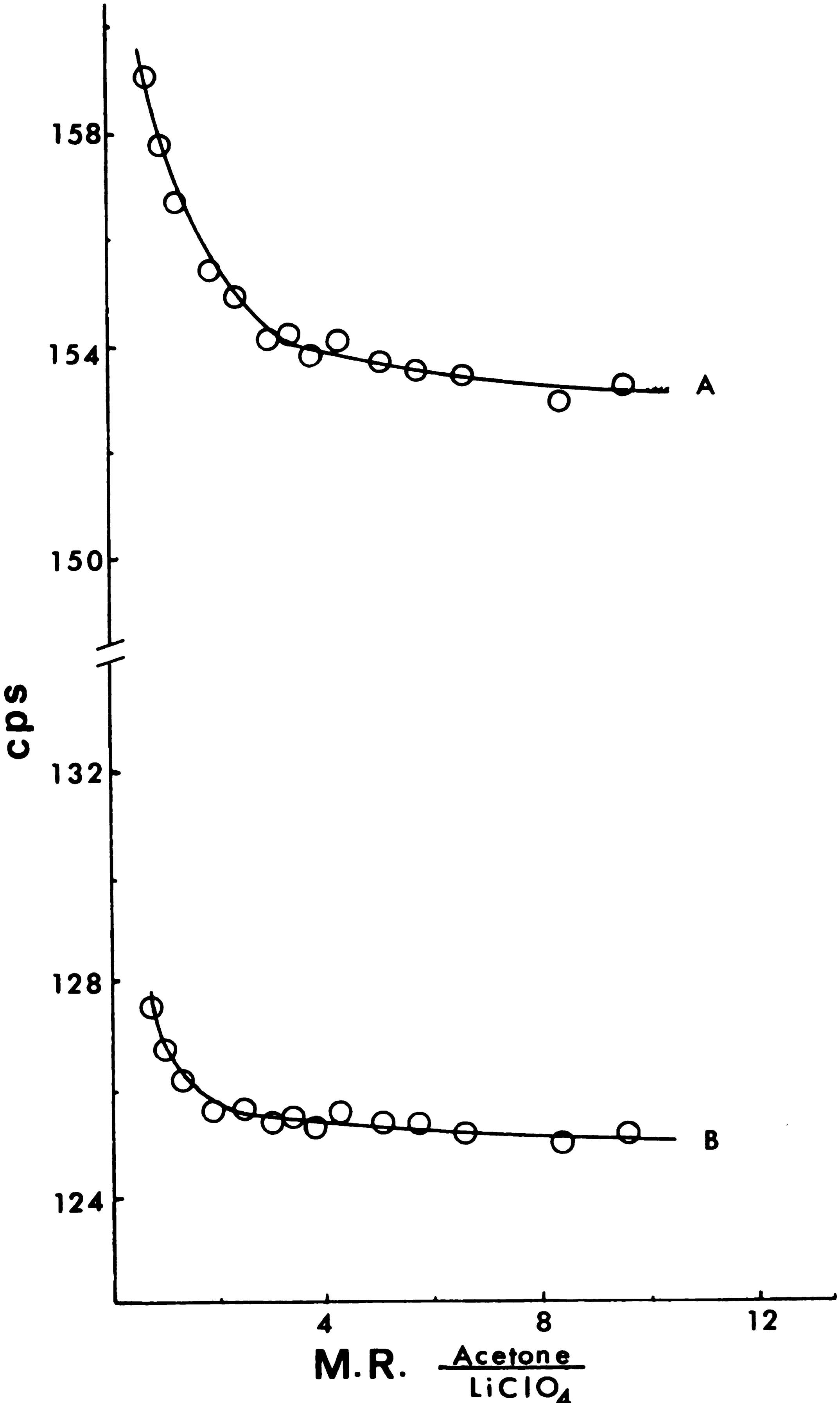
158
154
150
132
128
124
cps
A
B
4
8
12
M.R. $\frac{\text{Acetone}}{LiClO_4}$

Figure 30.

Table 20. Chemical Shifts (Hz) of Dimethyl Sulfoxide and Acetic Acid Protons in Solvent V

Salt	Conc (M)	Mole Ratio ($DMSO/LiClO_4$)	DMSO	Acetic Acid $-CH_3$	Acetic Acid $-COOH$
Blank	--	--	164.3	122.0	678.5
$LiClO_4$	0.178	11.30	165.5	122.9	679.5
	0.245	8.20	165.6	122.9	684.0
	0.284	7.07	165.2	122.9	680.0
	0.329	6.10	165.9	123.1	683.0
	0.376	5.34	165.7	123.0	680.0
	0.417	4.81	165.8	123.2	683.5
	0.486	4.13	166.1	123.4	681.0
	0.587	3.42	166.4	123.7	682.5
	0.695	2.89	166.5	123.9	678.0
	0.844	2.38	166.7	124.3	680.0
	1.05	1.92	167.4	124.8	675.0
	1.40	1.44	167.6	125.6	673.0
	1.70	1.20	167.5	126.1	664.0
	2.15	0.93	168.5	127.2	659.5
	3.17	0.6	169.2	128.8	634.5

Figure 31. Chemical shifts of the dimethyl sulfoxide and acetic acid protons vs. DMSO/$LiClO_4$ mole ratio in Solvent V. A. Hydroxyl proton of acetic acid. B. DMSO. C. Methyl protons of acetic acid.

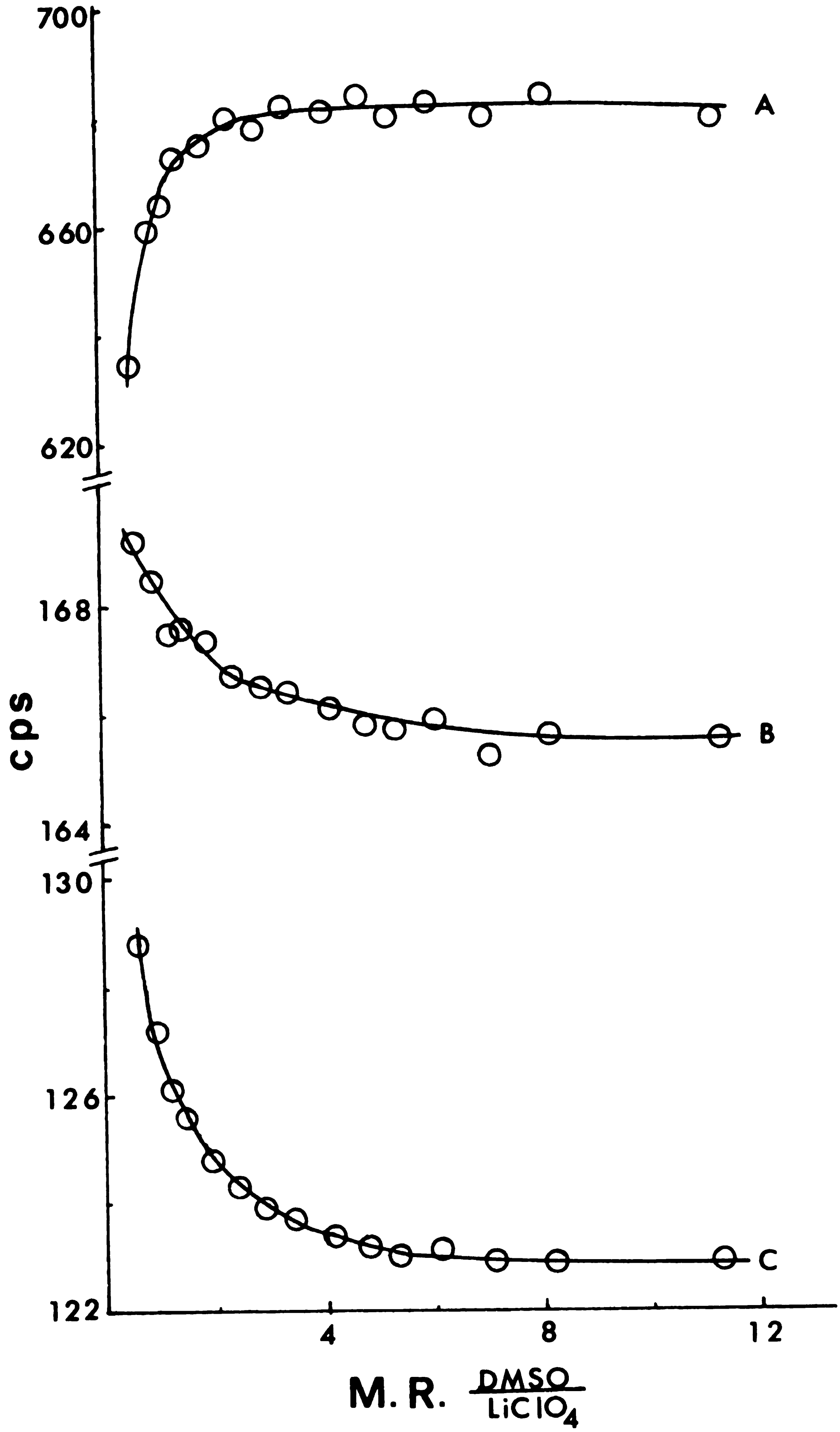
700
660
620
168
164
130
126
122
cps
A
B
C
4
8
12
M.R. $\frac{DMSO}{LiClO_4}$

Figure 31.

Table 21. Chemical Shifts (Hz) of Protons of Dimethyl Sulfoxide, Acetone and Nitromethane in Solvent VI

Conc. (M) $LiClO_4$	M.R. $(\frac{\text{DMSO + Acetone}}{LiClO_4})$	DMSO	Acetone	CH_3NO_2
Blank	--	149.8	124.5	260.0
0.0883	27.3	152.8	124.9	260.4
0.101	23.9	153.2	125.0	--
0.124	19.4	154.0	125.3	--
0.165	14.6	154.9	125.2	--
0.197	12.2	155.9	125.4	260.4
0.241	10.0	156.7	125.5	--
0.295	8.17	158.4	125.9	260.4
0.404	5.97	160.4	126.7	--
0.494	4.88	161.6	127.6	260.6
0.607	3.97	163.3	129.0	--
0.745	3.23	164.8	130.9	260.6
1.07	2.25	167.1	134.5	--
1.20	2.01	167.8	135.6	260.6
1.66	1.45	169.6	137.8	261.0
2.09	1.15	170.6	138.7	261.1
2.48	0.97	171.3	139.3	262.0
2.85	$\sim$0.8	171.7	139.5	262.5
3.59	$\sim$0.6	172.5	139.9	263.3

Figure 32. Chemical shifts of the nitromethane, dimethyl sulfoxide and acetone protons vs. (DMSO + Acetone)/$LiClO_4$ mole ratio in Solvent VI. A. CH_3NO_2. B. DMSO. C. Acetone.

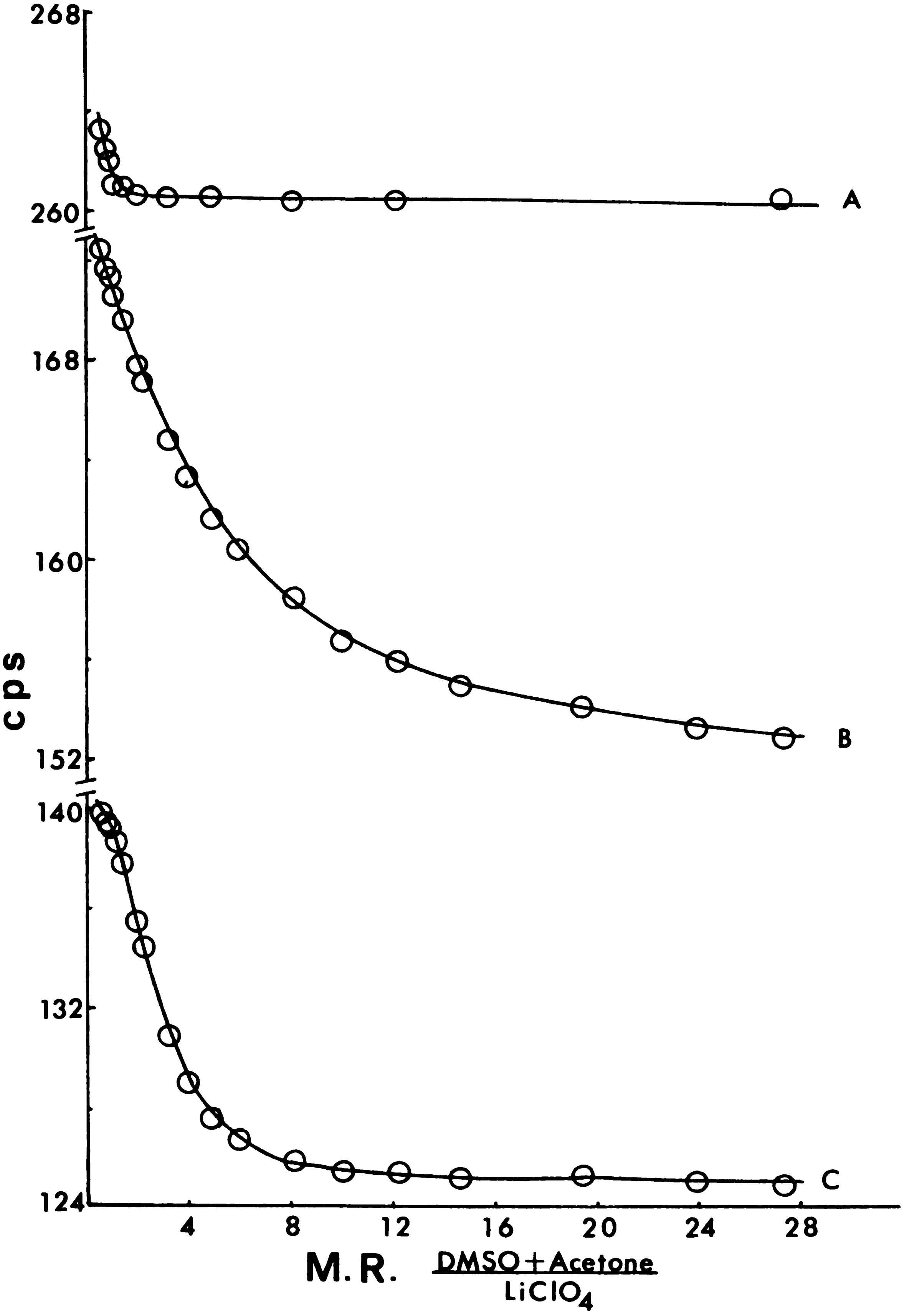
268
260
168
160
152
140
132
124
cps
A
B
C
4
8
12
16
20
24
28
M.R. DMSO+Acetone / LiClO4

Figure 32.

VI. SUMMARY AND CONCLUSION

Several nonaqueous solvents have been examined in this study: acetone, acetic acid, tetrahydrofuran, dimethyl sulfoxide and nitromethane. Most of the studies were carried out with lithium and sodium salts. Potassium, ammonium, rubidium, cesium and tetraalky - ammonium salts are also used, but to a lesser extent.

Two major factors are apparent in determining the formation of various solvated species and the general properties of electrolyte solutions: (1) the nature of the solvent, and (2) for the same cation, the nature of the anions. The effects of these two factors are reflected in results obtained in this study.

In acetone, the far infrared lithium-acetone vibrational bands are identical for the iodide and the polyatomic anion salts. In acetone-nitromethane mixtures the perchlorate ion Raman band is not affected by the lithium ion when acetone/Li^+ mole ratio is ≥ 4. Thus in these cases it is likely that the predominant solvated species are solvent-separated ion pairs, and the far infrared band arises from the vibration of the cation in a solvent cage. However, when the anions bromide or chloride are present in solution, due to their stronger affinity for the cation, they can successfully replace the solvent molecules in the solvation sphere, forming either contact ion pair or together with other remaining solvent molecules in the solvation sphere forming a near neighbor environment in which the cation vibrates. In either way the anion will exert an influence on the frequency of the far infrared band. Vapor phase osmometric measurements also indicate the same trend. In general, it is very likely that under identical conditions, solvent-separated ion pairs will be easier to dissociate than a contact ion pair. Thus, with few exceptions, the polyatomic anion salts of lithium and sodium show appreciable dissociation. However, no dissociation is observed for the bromide and chloride.

Nearly all the far infrared bands of the alkali metal salts in tetrahydrofuran are anion dependent. Due to low polarity of this solvent, the separation of the cation and anion by the solvent molecules is unlikely. However, tetrahydrofuran has a considerable donor ability for the cations (see Chapter II), and thus, the predominant solvated species in tetrahydrofuran solutions most likely will be solvent-shared ion pairs or solvated contact ion pairs. Vapor phase osmometry evidence show the same results. There is no appreciable dissociation observed for all the salts studied, and the apparent molecular weight of lithium chloride approaches that of a dimer.

In acetic acid solutions the far infrared bands of lithium salts are anion-independent, and a fluoride anion - acetic acid band, which is cation independent, is also observed. Thus although the polarity of acetic acid is low, the effect of hydrogen-bonding may play an important role in the formation of solvated species. It is likely that in acetic acid, unlike that in tetrahydrofuran, no appreciable contact ion pairs are formed, the predominant solvated species probably are either solvent-shared or solvent-separated ion pairs.

Mixed solvents studies indicate that, among the solvents studied, dimethyl sulfoxide is the strongest donor, acetone and acetic acid have about the same donor power, and nitromethane is the weakest donor.

VII. SUGGESTIONS FOR FUTURE STUDY

1. Solutions of silver and the alkaline-earth metal salts could be investigated by both infrared and Raman techniques for the possible existence of ionic or covalent bonding and their vibrations between the non-aqueous solvents and the various cations.

2. Conductance data for tetrahydrofuran and many other non-aqueous solvents are still rather sparse. Thus more conductance studies at both dilute and concentrated solutions (e.g., 0.5 to 1 M) would provide additional information about ionic association and dissociation.

3. Studies on the effect of pressure on the solvation band (10) should be extended to other salts (e.g., lithium bromide and lithium perchlorate) in tetrahydrofuran solutions. As discussed in Chapter V, the choice of lithium chloride might limit the conclusions drawn from the study. Results from studies of other salts would provide a wider basis for comparison. This type of study could also be extended to acetic acid, acetone and other solvents.

4. Thermoelectric vapor phase studies could be extended to other solvents, especially solvents with high dielectric constants. Temperatures higher than 37°C might be used for other solvents so as to achieve enough vapor pressure for osmometric measurements.

5. Fluorine nmr of various fluorides in acetic acid could be studied. The effect (or lack of it) of cations on the fluoride chemical shift would yield more information on the nature of the fluoride - acetic acid solvation band.

6. More mixed solvent systems could be studied by proton magnetic resonance, infrared, ^{23}Na and ^{7}Li nuclear magnetic resonance techniques.

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APPENDICES

APPENDIX 1

MISCELLANEOUS OBSERVATIONS

Silver Perchlorate in Acetone

Several solutions of silver perchlorate in acetone (from 0.4 to 0.8 M) were prepared and their far infrared spectra (600-100 cm^{-1}) were measured. The broad solvation bands observed for lithium and sodium salts were not detected in the silver perchlorate solutions. It was noted, however, that the 528 cm^{-1} acetone band had a shoulder at about 549 cm^{-1} which was resolved into a band when solvent absorption was subtracted. It can be assigned to the shifting of the acetone band at 528 cm^{-1} due to complexation (48). The splitting and shifting of the 528 cm^{-1} acetone band by silver perchlorate is larger than that observed in the case of lithium perchlorate, which indicates a stronger interaction between the silver ion and acetone. The 390 cm^{-1} acetone fundamental band was also broadened slightly, and after subtracting pure solvent absorption, a weak band at 403 cm^{-1} was observed. However, unlike the usual broad solvation bands observed for lithium and sodium, this band is narrow. The band probably arises from the splitting of the 390 cm^{-1} acetone band. In acetone solutions of lithium salts, the weak splitting of the 390 cm^{-1} acetone band may be incorporated into the more intense solvation band.

No appreciable broadening or the appearance of a shoulder were observed for the 390 cm^{-1} and 528 cm^{-1} acetone bands in sodium salt solutions of up to 1 M concentration.

Raman Spectra of Solutions of Acetone and Sodium Salts in Nitromethane

Sodium perchlorate and sodium tetraphenylborate were used to examine the effect of the sodium ion on the 789 cm^{-1} acetone Raman band. Several solutions with acetone/Na^+ mole ratio from 8:1 to 3:1 were prepared in nitromethane (cf. Chapter V, (A)), and the position of the 789 cm^{-1} acetone band was followed as a function of mole ratio. In contrast to the lithium salts (Figure 7), no splitting of the band was detected. However, a gradual shifting of the 789 cm^{-1} band was observed, and at acetone/Na^+ of about 3:1, the band maximum was at 799 cm^{-1}.

Nmr Mole Ratio Studies of Acetone with Sodium Tetraphenylborate in Nitromethane

Sodium tetraphenylborate was found to be soluble in nitromethane to about 0.5 M. Thus nuclear magnetic resonance mole ratio study was extended to the system acetone/$NaBPh_4$ in this solvent. The concentration of acetone was kept constant at 1.5 M, and the concentration of sodium tetraphenylborate was varied. The results are given in Table 22.

The direction of the chemical shifts is opposite to that observed in the acetone/Li^+ mole ratio studies. The large upfield shift for the nitromethane protons was also observed. No valid explanation for these shifts can be given at the present time. It is likely that the phenyl rings of the bulky tetraphenylborate anion may play an important role in affecting the chemical shifts of acetone and nitromethane protons.

Table 22. Effect of Sodium Tetraphenylborate on the Chemical Shifts (Hz) of Acetone and Nitromethane Protons

Mole Ratio (Acetone/$NaBPh_4$)	Acetone	Nitromethane
Blank (1.5 M acetone)	124.8	259.9
10.0	125.5	256.5
7.8	125.6	256.4
5.2	125.6	254.9
3.8	125.2	251.9
1.9	122.7	242.9

Effects of Molecular Sieve on Solvents

The use of molecular sieve for drying nonaqueous solvents and the storage of purified solvent over it is a widely accepted practice. However, it was found that molecular sieve had a catalytic effect on the decomposition of acetone and decomposition occurred after two months storage over molecular sieve. Molecular sieve was found to be slightly soluble in acetic acid. The solubility appeared to have a negative temperature coefficient. Thus when warming purified acetic acid which had been stored over molecular sieve for several months, fine particles appeared in the solvent.

It was found that when the solvents were stored in tightly capped bottles with the neck wrapped in Saran Wrap, no detectable increase in water content was noted after storage of 4 months.

APPENDIX II

Solubilities and Maximum Concentrations of Solutions Used in this Study

Table 23 lists the solubilities and the maximum concentrations of the salt solutions used in the present study. A salt is considered insoluble in the solvent if its solubility is less than 0.1 M. The saturation limit was deemed reached on two criteria: (1) When the salt at that concentration was barely dissolved after intermitten shaking for one hour and left in contact with solvent for one or two days; (2) the next higher concentration (generally about 0.2 M more concentrated) could not be prepared. A salt is listed as soluble (sol) if the solubility was found to be greater than 0.1 M; however, the spectrum of the salt solution was not measured.

Table 23. Solubilities and Maximum Concentrations (M) of Various Salts in the Solvents Used in this Study

Salt	Acetone	HOAc	THF	CH_3NO_2
LiF	Insol	Insol		
LiCl	0.1 (∼sat)	1.1 (∼sat)	0.5	
LiBr	1.0 (∼sat)	1.1 (∼sat)	0.3	
LiI	1.5	2.0 (∼sat)	0.4	
$LiNO_3$	0.6 (∼sat)	0.7	0.5	
$LiClO_4$	4.2	2.1 (∼sat)	1.8	0.2 (∼sat)

Table 23. (Continued)

Salt	Acetone	HOAc	THF	CH_3NO_2
LiSCN	0.6	2.3		
$LiBPh_4$	0.4	0.5	0.3	0.3
NaAc	Insol	0.5		
$NaNO_3$	Insol			
NaF	Insol	0.1		
$NaClO_4$	2.3 ($\sim$sat)	0.3 ($\sim$sat)		Insol
NaCl	Insol	0.1		
NaBr	Insol	Insol		
NaI	0.9	Sol		
NaSCN	0.6 ($\sim$sat)	0.4		
$NaBPh_4$	0.8			0.5 ($\sim$sat)
NH_4Br	Insol	Insol	Insol	
NH_4I	Insol	Insol		Insol
NH_4SCN	1.2	0.4		Sol
NH_4BPh_4	Insol	Insol		
KF	Insol	0.8		
KBr	Insol	Insol		
KCl	Insol	Insol		
KI	Insol	Insol		
$KClO_4$	Insol	Insol		
KSCN	0.9 ($\sim$sat)	0.6		Insol
KBF_4	Insol	Insol		
$KBPh_4$	Insol	Insol		
RbF	Insol	0.9		
RbCl	Insol	0.2		
$RbClO_4$	Insol	Insol		
$RbNO_3$	Insol	Insol		
$RbBPh_4$	Insol	Insol		
CsF	Insol	1.5		
CsCl	Insol	0.2		
CsBr	Insol	0.1 ($\sim$sat)		
CsSCN	Insol	0.1 ($\sim$sat)		
$CsNO_3$	Insol	Insol		
$CsBPh_4$	Insol	Insol		
$AgClO_4$	0.8			
$AgNO_3$	Insol			
Me_4NF		0.4		
Me_4NCl	Insol	0.5		
Et_4NCl	Insol	0.4		

Figure 23. (Continued)

Salt	Acetone	HOAc	THF	CH_3NO_2
Me_4NClO_4	Insol	Insol		
Bu_4NClO_4	1.0	Sol		
Bu_4NBr	0.8			
Pr_4NBr	0.5			
Bu_4I	1.0			