Lithium Salts as Solutes in Nonaqueous Media

Solubility Trends of Lithium Perchlorate

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THE ORIGIN of the exceptionally high solubility of anhydrous lithium perchlorate in organic solvents (26, 33, 34) has been a matter of some conjecture (24). This uni-univalent salt of a small cation and a large anion must possess a favorable balance of lattice and solvation energies conducive to extensive solubility in a wide range of solvents (21). Similar characteristics appear to be shown by lithium iodide, thiocyanate, and nitrate in a variety of media wherever chemical compatibility permits (23). The solubility and stability of lithium perchlorate have prompted its use in studies of salt effects in organic reactions (6, 35, 36).

Conductivity investigations have demonstrated the electrolytic properties of solutions of lithium perchlorate in such diverse materials as methanol (20), ethanol (20), cyclohexanol (16), nitromethane (37), diethyl ether (7), N,N-dimethylacetamide (20), hydrazine (29), pyridine (27), acetonitrile (28), and hydrogen cyanide (3). With the renewed interest in the nature of electrolyte solutions from the chemical or solvation point of view (2), it was felt that determination of the solubility trends of lithium perchlorate would yield some insight into its solution processes.

Modern concepts of organic chemistry have permitted the resolution of the relative charge densities on the component atoms of many types of molecules. This with considerations of hydrogen bonding and of steric hindrance have allowed for a development of the solubility trends of lithium perchlorate as a function of solvent structure. The interaction of lithium perchlorate with a solvent is viewed in this study primarily in terms of solute solvation proceeding from ion-dipole interaction. Here again as in the water (11) and liquid ammonia systems (14), the unusual solution properties of lithium and its compounds appear to stem from the high solvation energy of the lithium ion.

EXPERIMENTAL

Anhydrous lithium perchlorate was prepared (19) and analyzed by precipitation as nitron perchlorate. Analysis of product: ClO_4^-, 93.7% (calcd., 93.5%).

The solvents of Tables I and II were all reagent grade and wherever indicated were purified further by fractional distillation after drying over anhydrous calcium sulfate. The complexes were equilibrated at 25.0 ± 0.02° C., except for several maintained at 30.0 ± 0.02° C. to prevent solidification. Constancy of density or of refractive index was taken as the criterion for equilibrium. Solute content was analyzed by one of four methods:

I. Evaporation of the solvent, followed by prolonged vacuum drying of the residue at 150° C.
II. Precipitation as nitron perchlorate where interference from the solvent did not occur.
III. Precipitation as silver chloride after conversion of the perchlorate by fusion with anhydrous sodium carbonate in a platinum crucible.
IV. By difference after direct base titration of acidic solvents.

The analytical method applied to each solution is indicated in Tables I and II. Three determinations were generally made from two separate samples.

The mole fraction of $LiClO_4$ provides a more useful basis for solubility comparisons because of large variations in the molecular weights of the solvents. Values given for dielectric constants and for dipole moments of the various pure solvents are taken from tabulations (30). The solubility data of Willard and Smith (34) are included in Table I.

DISCUSSION

Inspection of Table II indicates no detectable solubility of lithium perchlorate in pure hydrocarbons or in chlorinated hydrocarbons. The latter materials despite their polar nature appear not to be able to provide centers of negative charge for association with the lithium ion. In the present studies, suitable dipoles stem from functional groups containing the more electronegative atoms, oxygen and nitrogen (18).

Lithium perchlorate displays fairly high solubility in the three normal aliphatic acids studied. There is considerable evidence to indicate interaction between acetic acid and the lithium ion. Thus, a number of lithium acetate–acetic acid solvates have been reported (5, 13), solvolysis of lithium perchlorate increases the hydrogen ion concentration of glacial acetic acid (17), and conductivity measurements (15) point to extensive solvation of the lithium ion in this medium coupled with ion-pair formation of salt solutes (12). The substitution of fluorine for hydrogen atoms on the methyl group of acetic acid decreases the electron-donor capacity of the carboxyl group by an electron-attracting inductive effect (9). Accordingly, the solubility of lithium perchlorate in trifluoroacetic acid is diminished in comparison with the other acids. Hydrogen bonding is prevalent among aliphatic acids (22) and may be significant in determining the solubility of lithium perchlorate in organic acids. This phenomenon involving the perchlorate group (20) and an unfavorable inductive effect may cause the low solvent power of acetic anhydride for lithium perchlorate.

A remarkable constancy of solubility was found for lithium perchlorate in benzyl alcohol and in the nine aliphatic alcohols listed in Table I. An average mole fraction content of solute of 0.354 ± 0.019 was determined. Positional isomerism involving primary or secondary alcohols produced but minor shifts in solubility. The poor solvent characteristics of tert-butyl alcohol are attributed to steric hindrance of effective ion-dipole interaction. It is particularly instructive to note the sharp decreases in solubility occasioned by attachment of the hydroxyl group to the aromatic nucleus as in m-cresol, when compared to a hydroxyl group held to a methylene radical as in the alkanols or benzyl alcohol. Participation of the hydroxyl group in resonance with the aromatic ring lowers the electron density on the oxygen atom making the oxygen a considerably poorer electron donor (10). Water is not as good a solvent for lithium perchlorate as are many of the alcohols. This may be due in part to the adverse energetics occasioned by the strongly intermolecular hydrogen-bonded water structure. The solubility of lithium perchlorate in water at 25° C. is 0.092 mole fraction of $LiClO_4$ (34).

The solubility of lithium perchlorate in substituted ammonias generally follows the base strength of the amine or the electron-donating capacity of the nitrogen atom. This charge density is increased by the degree of substitution of alkyl groups on the ammonia molecule and decreased, as in aniline, by resonance with the aromatic ring, or by multiple bonding to carbon as in pyridine (32). Thus, the observed order of solubility for all but the sterically hindered amines (tert-butylamine and tributylamine) is: alkyl amines

$(K_b \sim 10^{-3}$ to $10^{-5}) >$ pyridine $(K_b = 1.7 \times 10^{-9}) >$ aniline $(K_b = 3.8 \times 10^{-10})$. The presence of N-methyl groups in aniline further decreases the observed solubility. Lithium

perchlorate forms solid ammoniates $(8, 25)$ indicative of ion-dipole interaction with ammonia.

Ethers, unlike acids, alcohols, and amines, are regarded

Table I. Solubility of Lithium Perchlorate in Organic Solvents at 25° C.

Solvent	LiClO₄, G./100 G. Solvent	Mole Fraction LiClO₄	Dielectric Constant	Dipole Moment, Debyes
Acids				
Acetic[a]	108.7 ± 0.1	0.380	6.15 (20°)	0.83
Trifluoroacetic[a]	11.7 ± 0.0	0.111	39.5 (20°)	2.28
Butyric[a]	60.0 ± 0.3	0.332	2.97 (20°)	0.63
n-Octanoic[a]	32.1 ± 0.3	0.303	...	...
Alcohols				
Methyl[b]	182.3	0.354	32.6 (25°)	1.66
Ethyl[b]	151.8	0.397	24.3 (25°)	1.68 (vapor)
n-Propyl[b]	105.0	0.372	20.1 (25°)	1.66
Isopropyl[c]	112.1 ± 0.1	0.388	18.3 (25°)	1.68 (vapor)
n-Butyl[b]	79.3	0.356	17.1 (25°)	1.68
sec-Butyl[c]	77.1 ± 0.1	0.349	15.8 (25°)	...
Iso-butyl[b]	58.1	0.288	...	...
tert-Butyl[d] (30°)	0.6 ± 0.0	...	...	...
1-Octanol[d,e]	43.8 ± 0.1	0.349	10.3 (20°)	1.68
2-Octanol[d]	44.7 ± 0.2	0.354	...	...
Cyclohexanol[d,e]	5.9 ± 0.1	0.053	15.0 (25°)	1.9
Benzyl[d,c]	49.8 ± 0.3	0.336	13.1 (20°)	1.66
Ethylene glycol[c]	96.7 ± 0.4	0.361	...	...
Amines				
n-Propyl[d,e]	59.1 ± 0.3	0.247	...	1.26
n-Butyl[c,e]	45.7 ± 0.3	0.239	5.3 (21°)	1.40
sec-Butyl[c,e]	45.7 ± 0.2	0.239	...	1.28
tert-Butyl[c,e]	10.7 ± 0.3	0.068	...	...
Dibutyl[d]	45.6 ± 0.4	0.356	...	...
Tributyl[d]	0.4 ± 0.0	...	...	...
Cyclohexylamine[d,e]	16.9 ± 0.1	0.136	5.37 (−21°)	1.32
Pyridine[c,e]	8.7 ± 0.1	0.061	12.3 (25°)	2.20
Aniline[d,e]	6.1 ± 0.2	0.051	6.89 (20°)	1.51
N-methylaniline[d]	1.4 ± 0.1	...	...	...
N,N-dimethylaniline[d]	0.1 ± 0.0	...	...	...
Ethylenediamine[d]	48.0 ± 0.3	0.213	14.2 (20°)	1.90
Esters				
Ethyl acetate[d]	95.1	0.441	6.02 (25°)	1.81
Ethyl benzoate[d]	29.2 ± 0.2	0.292	6.02 (20°)	1.99
Diethyl carbonate[c,e]	52.6 ± 0.1	0.369	2.82 (20°)	...
Diethyl sebacate[d]	21.3 ± 0.1	0.340	...	...
Diethyl phthalate[d]	5.5 ± 0.0	0.012	...	...
n-Butyl nitrite[e,f]	3.4 ± 0.0	0.032	...	...
Benzyl acetate[d]	50.1 ± 0.4	0.414	5.1 (21°)	1.80
Ethyl acetoacetate[d]	76.7 ± 0.1	0.484	...	...
Ethers				
Diethyl[b]	113.7	0.442	4.34 (20°)	1.15
n-Butyl[c,e]	13.6 ± 0.2	0.143	3.06 (25°)	1.22
Tetrahydrofuran[c,e]	27.1 ± 0.2	0.155	...	...
p-Dioxane[e,f]	0.2 ± 0.1	...	2.21 (25°)	0.45
Anisole[d]	0.1 ± 0.0	...	4.33 (25°)	1.20
Propylene oxide[d]	91.4 ± 0.6	0.333	...	1.98
Ketones and aldehydes				
Acetone[b]	136.5	0.427	20.7 (25°)	2.72
Cyclopentanone[d,e]	63.8 ± 0.2	0.335	...	...
Cyclohexanone[d,e]	54.0 ± 0.3	0.332	18.3 (20°)	2.8
Propionaldehyde[d,e]	110.5 ± 0.7	0.376	78.5 (17°)	2.57
Benzaldehyde[d]	51.5 ± 0.3	0.339	17.8 (20°)	2.77
Miscellaneous compounds with functional groups				
Acetonitrile[e,f]	16.3 ± 0.1	0.059	37.5 (20°)	3.37
Benzonitrile[d]	21.9 ± 0.2	0.175	25.2 (25°)	4.05
Nitrobenzene[e,f]	0.2 ± 0.0	...	34.8 (25°)	3.99
Formamide[c,e]	142.1 ± 0.2	0.376	109.5 (25°)	3.37
N,N-Dimethylformamide[c,e]	75.0 ± 0.2	0.340	...	...
Acetic anhydride[d]	8.1 ± 0.0	0.072	20.7 (19°)	2.8
2-Ethoxyethanol[d,e]	136.6 ± 0.4	0.536	...	2.08
2-Aminoethanol[c]	78.9 ± 0.9	0.312	...	...
m-Cresol[d,e]	8.5 ± 0.0	0.079	11.8 (25°)	1.54

[a] Method IV. [b] Data of Willard and Smith (34). [c] Method II. [d] Method III. [e] Dried and redistilled solvent. [f] Method I.

Table II. Solvents Exhibiting No Detectable Solvent Power for Lithium Perchlorate

(0.0 ± 0.0 Grams LiClO₄ per 100 Grams Solvent at 25°)

Solvent	Dielectric Constant	Dipole Moment, Debyes
Hydrocarbons		
n-Heptane[a,b]	1.92 (20°)	0
1-Octene[a,b]	...	...
Cyclohexane[a,b]	2.02 (20°)	0
Cyclohexene[a,b]	2.22 (25°)	...
Benzene[a,b]	2.28 (20°)	0
Toluene[a,b]	2.38 (25°)	0.4
Xylene[a,b]	...	...
Tetrahydronapthalene[c]	...	...
Decahydronaphthalene[c]	2.26 (20°)	...
Miscellaneous Compounds with Functional Groups		
Chloroform[a,b]	4.8 (21°)	1.15
Carbon tetrachloride[a,b]	2.24 (20°)	0.0
Chlorobenzene[a,b]	5.62 (25°)	1.56
n-Propyl nitrate[a,b]	...	...
Furan[b,d]	...	0.67
Diphenyl ether[c] (30°)	...	...
Hexachloroacetone[a,b]	...	...

[a] Method I. [b] Dried, redistilled solvent. [c] Method III. [d] Method II.

as virtually devoid of hydrogen bonding (22). Accordingly, solvation of lithium perchlorate in ethers is due primarily to ion-dipole attractions as modified by steric hindrance effects. The electron densities of the oxygen atoms in furan, anisole, and diphenyl ether are greatly diminished by resonance with resultant low solvent powers for lithium perchlorate (1, 32). In addition, anisole and diphenyl ether probably engender considerable steric hindrance about the oxygen atom. The relatively nonpolar character of p-dioxane inhibits solubility. Tetrahydrofuran and propylene oxide, in contrast to furan, are good solvents for lithium perchlorate. The drop in solubility in passing from diethyl ether to dibutyl ether is perhaps a steric phenomenon. The effect of hydrogen bonding in determining solubility is believed to be demonstrated by the relative insolubility of lithium perchlorate trihydrate in diethyl ether (0.2 weight % at 25°) (34). Crystal structure studies of the hydrated salt show a continuous network of hydrogen bonding with the perchlorate groups and ion-dipole orientation between the lithium ion and water molecules (31). Thus, diethyl ether as a solvent is unable to compete with water on the bases of both cation and anion solvation.

The substitution of chlorine for hydrogen in acetone produces no detectable solubility of lithium perchlorate in hexachloroacetone because of an unfavorable inductive effect and possibly, steric hindrance. The attachment of highly electron-withdrawing groups such as aldehyde or nitrile to either an alkyl group or an aromatic nucleus does not appreciably affect solubility. This is to be expected, inasmuch as the transition from alkyl to aromatic linkage does not involve any decrease in electron density of these functional groups as with hydroxyl and amino groups. For meta-directing groups on the aromatic nucleus, resonance is a favorable factor in maintaining and even increasing charge concentration.

Decrease in solubility of lithium perchlorate from formamide to N,N-dimethylformamide may be due to strongly diminished hydrogen bonding in the latter (4).

Present studies have considerably extended the range of solvents available for lithium perchlorate. Solubility is not dependent solely on the presence of an oxygen-containing functional group; amines and nitriles are effective solvents as well. The overriding principle in delineating solubility trends appears to be the presence of high negative charge centers in the solvent molecules which can lead to favorable

ion-dipole interactions. Hydrogen bonding and steric hindrance may also be important in determining the solubility of lithium perchlorate in a particular medium. Solvent structure information from the currently recognized generalizations of organic chemistry appears to be more helpful in interpreting solvent-solute interaction than in considering a macroscopic property of the pure solvent such as the dielectric constant or dipole moment.

A review of the literature has revealed no extensive polythermal investigation of lithium perchlorate with an organic solvent. On the basis of present studies, compound formation can be anticipated for many of these systems.

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