Conductivity and Viscosity of Lithium Perchlorate in Mixed Nonaqueous Solvents at Various Temperatures

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Relative viscosities and conductivities of lithium perchlorate ($LiClO_4$) have been investigated in mixed nonaqueous solvents of high permittivity and low viscosity at 10, 20, 30, 40, and 50 °C. γ-Butyrolactone (γ-BL), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were used as high-permittivity solvents, and 1,2-dimethoxyethane (DME) was used as a low-permittivity and low-viscosity solvent. Conductivity of $LiClO_4$ in the solvent system was improved by 1,2-dimethoxyethane and showed a maximum at 25-50 wt % of 1,2-dimethoxyethane. The conductance maxima for 1 mol dm^{-3} $LiClO_4$ increased in the order DME > DMF > DMSO for systems containing γ-BL. The results are interpreted qualitatively and demonstrate the use of $LiClO_4$ in γ-BL + DME solvents as a potential electrolyte system for practical lithium batteries.

Introduction

Solute-solvent studies involving electrolytes have been a subject of interest to solution chemists for quite sometime (*1-5*). Such studies on the transport properties of electrolytes in aqueous and nonaqueous solvents are of interest in various technologies like high energy density batteries, photoelectrochemical cells, electrodeposition, and wet electrolytic capacitors and in electroorganic synthesis (*6*).

A literature survey (*7*, *8*) suggests that the use of mixed solvents involving high permittivity, low viscosity, and wide liquid range is practicable for use in high energy density batteries, especially lithium batteries. The advantages of using mixed solvents over their purer counterparts in lithium batteries is to manipulate the suitable properties of these solvents for fulfilling the above conditions. Recently, Matsuda et al. (*9*) have reported the transport properties of lithium salts in propylene carbonate + 1,2-dimethoxyethane, sulfolane + 1,2-dimethoxyethane, and dimethyl sulfoxide + 1,2-dimethoxyethane solvent systems at 30 °C and suggested the use of lithium hexafluorophosphate in sulfolane + 1,2-dimethoxyethane or dimethyl sulfoxide + 1,2-dimethoxyethane in fabricating practical lithium batteries. In the present paper, the conductance and viscosity behavior of lithium perchlorate in three mixed-solvent systems has been compared qualitatively.

It is known that aprotic solvents show high permittivities, low viscosities, and strong temperature dependence (*7*). Hence in order to develop suitable mixed solvents fulfilling the conditions mentioned above, we have chosen mixtures of aprotic protophilic solvents, viz., *N,N*-dimethylformamide and dimethyl sulfoxide, an aprotic protophobic solvent, i.e., γ-butyrolactone, and a low-viscosity solvent, i.e., 1,2-dimethoxyethane, thereby balancing the drawbacks of the pure solvents. The conductivity of lithium perchlorate in different solvent systems (γ-butyrolactone + dimethyl sulfoxide; γ-butyrolactone + *N,N*-dimethylformamide; γ-butyrolactone + 1,2-dimethoxyethane) are at first explained in terms of solution viscosity and then on the donor-acceptor properties of the solvents (*10*), which mainly govern the ion-solvent interactions.

Comprehensive investigations on the solvation of ions in different organic solvents are scanty (*6*). However, some data are available at moderate concentrations of these salts. The main purpose of the present study is to develop suitable electrolyte solutions for use in practical lithium batteries.

Experimental Section

Relative viscosities were calculated according to

$$\eta_r = \rho t/\rho_0 t_0 \tag{1}$$

where ρ is the density and t is the flow time. The subscript 0 refers to values for the solvent. Viscosities of solutions were measured with a Cannon-Fenske direct-flow viscometer, as described in our earlier publications (*3*, *4*). The kinetic energy correction term for the viscometer fell in the region of experimental error and was therefore neglected. From the minimum of three consecutive flow times which were averaged for each solution, the reproducibility was usually better than 0.01%. The relative viscosities determined were precise to 0.03% (*3*, *4*). Densities of the solutions were measured with pycnometers, as described earlier (*3-5*). The values are precise to $\pm 5 \times 10^{-5}$ g cm^{-3}.

Conductance measurements were made by means of Wayne Kerr autobalance precision bridge B331/MK 11 with an accuracy of ±0.01 % and $\omega = 10^4$ rad/s using a standard dip type conductivity cell. The cell constant was 0.796. The conductivity cell was standardized with use of 0.1 and 0.01 D KCl solutions and agreed well with the literature values. Taking account of the purity of the solute and solvents used and the method of measurements employed, the overall accuracy of the conductance measurements is ±0.05%.

Materials

All solvents and electrolytes were purified as described below (*11*).

γ-Butyrolactone of Analytical Grade (Merck) with a quoted purity of >99% was stored over calcium oxide and then distilled under vacuum.

Dimethyl Sulfoxide of Analytical Grade (Koch-light Laboratories Ltd.) with a quoted purity of >99.5% was dried over molecular sieves and distilled under vacuum below 50 °C.

N,N-Dimethylformamide of Analytical Grade (BDH) with a quoted purity of >99% was stored over potassium hydroxide and then distilled under vacuum.

1,2-Dimethoxyethane of Analytical Grade (Fluka) with a quoted purity of >99% was distilled over lithium metal under vacuum and then stored over molecular sieves.

All the above solvents contained less than 100 ppm water. Aquatest 8 was used for estimation of water. Lithium per-

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Table I. Dielectric Constant (D), Viscosity (η_0/cP), and Donor Number (DN) of Different Nonaqueous Solvents at 25 °C

solvent	property		
	D	η_0	DN
γ-butyrolactone	39.1	1.75	18
dimethyl sulfoxide	46.6	1.99	29.8
N,N-dimethylformamide	39.7	0.796	26.6
1,2-dimethoxyethane	7.20	0.455	24

Table II. Viscosities for γ-Butyrolactone + Dimethyl Sulfoxide Solvent Mixtures at Various Temperatures

temp/°C	η at various wt % γ-BL/cP				
	100	75	50	25	0
10	3.05	3.30	3.34	3.43	
20	1.91	1.98	1.98	2.08	2.27
30	1.27	1.31	1.29	1.36	1.47
40	0.85	0.82	0.80	0.90	0.92
50	0.60	0.59	0.58	0.64	0.65

Table III. Viscosities for γ-Butyrolactone + *N,N*-Dimethylformamide Solvent Mixtures at Various Temperatures

temp/°C	η at given wt % γ-BL/cP				
	100	75	50	25	0
10	3.05	2.45	2.01	1.74	1.47
20	1.91	1.51	1.22	1.07	0.95
30	1.27	0.99	0.83	0.71	0.60
40	0.85	0.65	0.53	0.46	0.39
50	0.60	0.47	0.40	0.33	0.30

Table IV. Viscosities for γ-Butyrolactone + 1,2-Dimethoxyethane Solvent Mixtures at Various Temperatures

temp/°C	η at given wt % γ-BL/cP				
	100	75	50	25	0
10	3.05	2.24	1.59	1.17	0.85
20	1.91	1.34	0.98	0.76	0.52
30	1.27	0.93	0.65	0.52	0.37
40	0.85	0.61	0.43	0.35	0.24
50	0.60	0.45	0.32	0.25	0.18

chlorate (Fluka, AG; Purum >99%) was used under vacuum for 24 h at 150 °C. The solutions were prepared inside a glovebox under dry atmosphere.

Results and Discussion

The relative viscosities and conductivities of 1 M $LiClO_4$ at 10, 20, 30, 40, and 50 °C were determined in 0, 25, 50, 75, and 100 wt % of γ-butyrolactone + *N,N*-dimethylformamide, γ-butyrolactone + 1,2-dimethoxyethane, and γ-butyrolactone + dimethyl sulfoxide binary mixtures. Data on the physical constants of pure solvents (γ-butyrolactone, 1,2-dimethoxyethane, *N,N*-dimethylformamide, and dimethyl sulfoxide) and mixtures (γ-butyrolacetone + dimethyl sulfoxide, γ-butyrolactone + *N,N*-dimethylformamide, and γ-butyrolactone + 1,2-dimethoxyethane) are presented in Tables I–IV, respectively. It is seen from Tables II–IV that the viscosities of γ-butyrolactone + *N,N*-dimethylformamide and γ-butyrolactone + 1,2-dimethoxyethane mixtures decrease with increases in *N,N*-dimethylformamide and 1,2-dimethoxyethane contents, respectively, in the entire composition and temperature range studied. However, in the case of the γ-butyrolactone + dimethyl sulfoxide solvent system, we observe a completely different trend, viz., a minimum is observed at 50–70 wt % of dimethyl sulfoxide concentration at all temperatures. The above observations could be attributed to the favorable combination of low-viscosity solvents (1,2-dimethoxyethane and *N,N*-dimethylformamide) with the high permittivity of γ-butyrolactone. However, in the case of dimethyl sulfoxide, since the viscosities and permittivities are similar, as in the case of γ-butyrolactone, only a marginal change in the viscosity of the solvent system is observed. The viscosities of lithium perchlorate (Figures 1–3) in all three mixed-solvent systems and the temperatures are higher than in the pure-solvent mixtures. The order of increase is dimethyl sulfoxide > *N,N*-dimethylformamide > 1,2-dimethoxyethane and could probably be due to high viscosity and preferential solvation of Li^+ ions by dimethyl sulfoxide. This aspect will be discussed at a later stage.

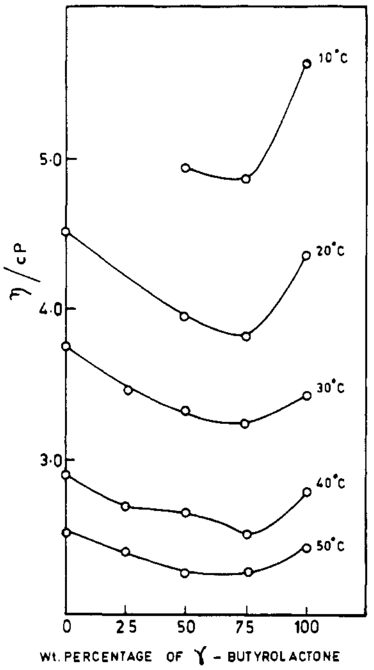

Figure 1. Variation of viscosity (η) of 1 M $LiClO_4$ in γ-BL + DMSO mixtures at different temperatures.

Table V. Specific Conductivity for Lithium Perchlorate in γ-Butyrolactone + 1,2-Dimethoxyethane at Various Temperatures

temp/°C	Λ at given wt % γ-BL/(10^{-2} S cm^{-1})				
	100	75	50	25	0
10	0.93	1.19	1.31	1.28	0.85
20	1.12	1.51	1.55	1.44	0.91
30	1.30	1.65	1.75	1.57	0.97
40	1.48	1.85	1.88	1.75	1.01
50	1.75	2.04	2.08	1.86	1.05

Table VI. Specific Conductivity for Lithium Perchlorate in γ-Butyrolactone + Dimethyl Sulfoxide at Various Temperatures

temp/°C	Λ at given wt % γ-BL/(10^{-2} S cm^{-1})				
	100	75	50	25	0
10	0.93	1.07	0.97	0.90	0.83
20	1.12	1.21	1.18	1.34	1.06
30	1.30	1.41	1.42	1.37	1.30
40	1.48	1.63	1.67	1.65	1.56
50	1.75	1.87	1.88	1.88	1.85

Table VII. Specific Conductivity for Lithium Perchlorate in γ-Butyrolactone + *N,N*-Dimethylformamide at Various Temperatures

temp/°C	Λ at given wt % γ-BL/(10^{-2} S cm^{-1})				
	100	75	50	25	0
10	0.93	1.13	1.33	1.47	1.65
20	1.12	1.36	1.58	1.77	1.95
30	1.30	1.65	1.85	2.06	2.19
40	1.48	1.85	2.08	2.35	2.49
50	1.75	2.07	2.37	2.59	2.81

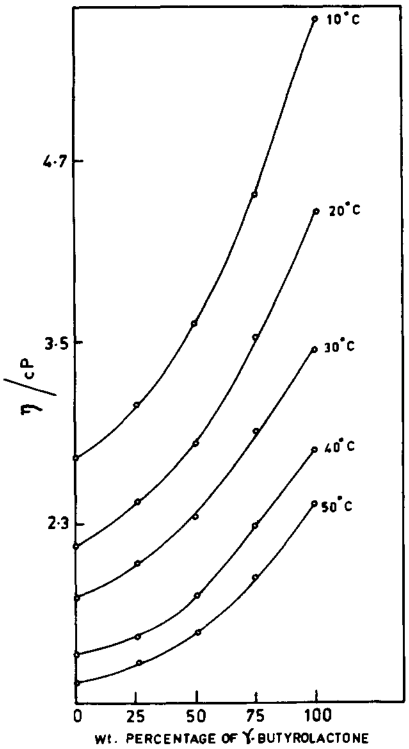

Figure 2. Variation of viscosity (η) of 1 M $LiClO_4$ in γ-BL + DMF mixtures at different temperatures.

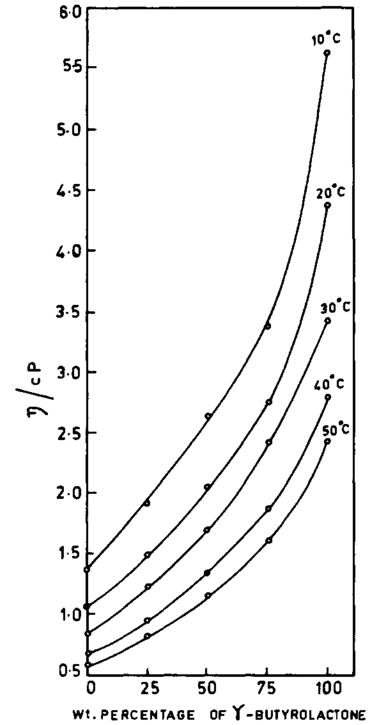

Figure 3. Variation of viscosity (η) of 1 M $LiClO_4$ in γ-BL + DME mixtures at different temperatures.

In Figure 4, a comparative representation of the variation of molar conductivity (Λ) of 1 mol dm^{-3} lithium perchlorate in γ-butyrolactone + 1,2-dimethoxyethane, γ-butyrolactone + *N*,*N*-dimethylformamide, and γ-butyrolactone + dimethyl sulfoxide at 30 °C as a function of γ-butyrolactone is presented. Specific conductivities of lithium perchlorate (Tables V–VII) in all three mixed-solvent systems are higher than those for pure solvents and show maxima for γ-butyrolactone + 1,2-dimethoxyethane and γ-butyrolactone + dimethyl sulfoxide solvent systems at all temperatures studied. Barthel et al. (*6*, *7*) from

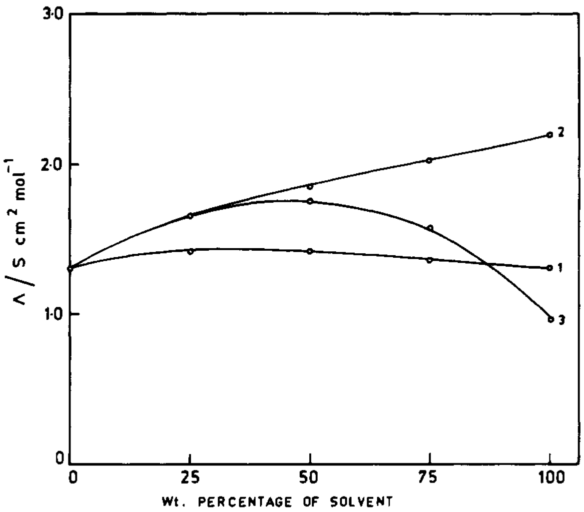

Figure 4. Variation of molar conductivity (Λ) of 1 M $LiClO_4$ with solvent composition at 30 °C: (1) γ-BL + DMSO; (2) γ-BL + DMF; (3) γ-BL + DME.

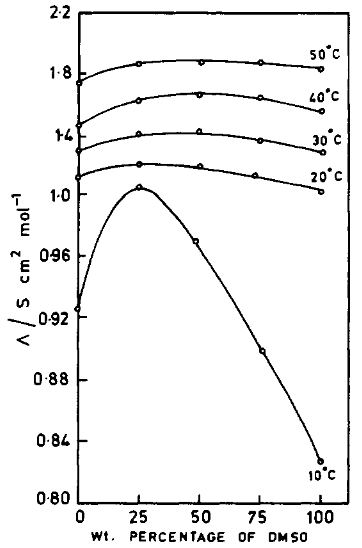

Figure 5. Variation of Λ of 1 M $LiClO_4$ in γ-BL + DMSO mixtures at various temperatures.

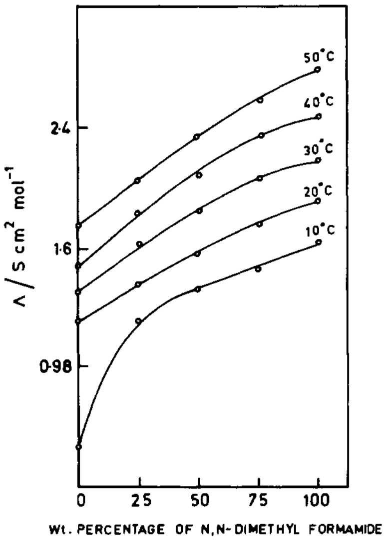

Figure 6. Variation of Λ of 1 M $LiClO_4$ in γ-BL + DMF mixtures at various temperatures.

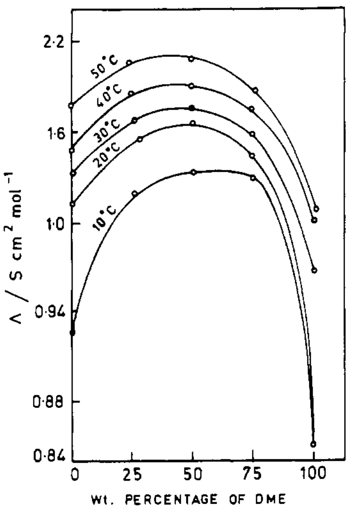

Figure 7. Variation of Λ of 1 M $LiClO_4$ in γ-BL + DME mixtures at various temperatures.

a comprehensive study of conductivity and viscosity of lithium hexafluoroarsenate in propylene carbonate + 1,2-dimethoxyethane mixtures at various temperatures observed similar effects and suggested that it is due to the consequence of competing effects, increasing charge density and decreasing ion mobility with an increase in electrolyte concentration. In the present case (Figures 5–7), we observe a well-defined conductance maximum for γ-butyrolactone + 1,2-dimethoxyethane while only a marginal maximum in γ-butyrolactone + dimethyl sulfoxide and no maximum in the case of γ-butyrolactone + *N*,*N*-dimethylformamide mixtures. However, at 10 °C an unusual well-defined conductance maximum is seen in the case of γ-butyrolactone + dimethyl sulfoxide, probably due to the smaller size of the solvated Li^+ ion.

Gutmann (*10*) defined donor number (DN) as the negative ΔH value (kcal mol^{-3}) for the reaction in 1,2-dichloroethane:

$$D + SbCl_5 \rightarrow D{\cdot}SbCl_5 \qquad (2)$$

where D denotes the solvent in question. As $SbCl_5$ is a strong electron acceptor, DN is a measure of the nucleophilic property of the solvent. However, acceptor number (AN) is derived from the chemical shift of ^{31}P NMR of Et_3PO, in the solvent under consideration. Acceptor number is expressed by a relative value while that of hexane is defined as 0, and the δ value of the $Et_3PO{-}SbCl_5$ adduct in 1,2-dichloroethane is arbitarily normalized as 100. Thus, acceptor number is a measure of the electrophilic property of the solvent (*9*).

From Table I (*12*), it is clear that donor number decreases in the order dimethyl sulfoxide > *N*,*N*-dimethylformamide > 1,2-dimethoxyethane > γ-butyrolactone. Thus, specific solvation of γ-butyrolactone to Li^+ ions would not be expected in the present three solvent systems investigated. Walden products ($\eta\Lambda$) for lithium perchlorate in the solvent mixtures at 30 °C are presented in Figure 8 and show similar behavior and decrease gradually for low-viscosity solvents (*N*,*N*-dimethylformamide and 1,2-dimethoxyethane). However, in γ-butyrolactone + dimethyl sulfoxide, we observe only a marginal increase, probably due to the high-viscosity and -permittivity of both solvents. Hence, viscosity contributes to the conductance of the solvent system. A similar decreasing trend was observed by Matsuda et al. (*9*).

Therefore, the use of lithium perchlorate in the γ-butyrolactone + 1,2-dimethoxyethane solvent system can be a probable electrolyte solution for lithium batteries.

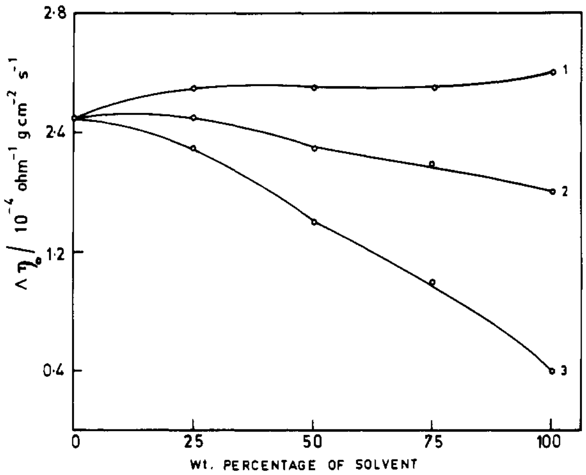

Figure 8. Variation of Walden product ($\Lambda\eta$) of 1 M $LiClO_4$ with solvent composition at 30 °C: (1) γ-BL + DMSO; (2) γ-BL + DMF; (3) γ-BL + DME.

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Nomenclature

γ = gamma
η = viscosity
ρ = density
t = flow time
ω = frequency
ppm = parts per million
Λ = conductivity
δ = delta
DN = donor number
AN = acceptor number
D = dielectric constant

Registry No. DMF, 68-12-2; DMSO, 67-68-5; γ-BL, 96-48-0; DME, 110-71-4; $LiClO_4$, 7791-03-9.

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