

Conductivity and viscosity studies of dimethyl sulfoxide (DMSO)-based electrolyte solutions at 25 °C

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Abstract

The specific conductivities and viscosities of lithium perchlorate at four different concentrations in dimethyl sulfoxide (DMSO)-based, binary mixed solvents are reported at 25 °C. The co-solvents are tetrahydrofuran (THF), 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL). The change in viscosity with solvent composition in all three mixed-solvent systems without electrolyte indicates the occurrence of structural disruption. The observed increase in viscosity with increase in LiClO_4 concentration suggests an increasing compactness of the structure. A 2 M LiClO_4 solution shows maximum conductivity at 20 vol.% DMSO in DMSO+DOL and at 40 vol.% DMSO in DMSO+THF mixtures. By contrast, a 1.5 M LiClO_4 solution has maximum conductivity at 40 vol.% DMSO in DMSO+DME mixtures. Preferential solvation of LiClO_4 by DMSO occurs in the respective mixtures with THF, DME and DOL.

Introduction

Several combinations of mixed, non-aqueous solutions containing lithium salts have been examined [1, 2] for their suitability as electrolytes in both primary and secondary lithium batteries. The successful use of mixtures of a high dielectric ester with a low viscosity ether – to obtain the best conducting electrolyte solution – has also been demonstrated [3, 4].

Dimethyl sulfoxide (DMSO)-based electrolyte solutions are considered [5–8] as promising candidates for use in lithium batteries. Nevertheless, there have been only a few investigations of the electrolytic properties and the lithium charge/discharge cycling behaviour in DMSO-based solutions [6]. Also, studies on structural aspects of DMSO-based solutions are lacking. This is remarkable since, in order to evaluate the best solution for lithium batteries, it is necessary to understand the structural changes that occur due to ion–solvent interactions. These interactions influence electrolytic properties such as the conductivity and viscosity.

To bridge this gap in the knowledge of such structural changes, the work reported here has involved a study of the viscosity and conductivity of DMSO-based solutions. The co-solvents are tetrahydrofuran (THF), 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL). The conductivity and viscosity of LiClO_4 has been investigated at four different concentrations, viz., 0.5, 1.0, 1.5 and 2.0 M in the binary mixtures over the entire solvent composition range at 25 °C. The conductivity and viscosity variations are interpreted in terms of system-specific, ion–solvent interactions.

Experimental

Materials

DMSO (Sarabhai) was kept at 70 °C on anhydrous potassium hydroxide pellets for 3 h and then distilled carefully under reduced pressure [9].

THF (E. Merck) was allowed first to stand for 48 h over freshly fused sodium hydroxide, and then for 24 h over sodium wire and refluxed. It was fractionally distilled in an atmosphere of dry nitrogen, and finally distilled from lithium aluminium hydride under vacuum [10].

DME (Fluka) was treated with lithium aluminium hydride, then fractionally distilled and stored over molecular sieves [11].

DOL (Fluka) was refluxed for 2 h with lead(IV) oxide, cooled and filtered. Xylene and more lead(IV) oxide were added and the mixture was fractionally distilled. The main fraction, collected at 70 to 71 °C, was treated with xylene and sodium wire and then redistilled. More sodium was added to the product and, finally, a sample that boiled at 74 to 75 °C was collected [12].

As all these solvents are highly hygroscopic, they were stored after purification in a glove box that was flooded with argon. The water content in the purified solvents was estimated to be around 60 ppm, as measured by AQUATEST 8 (USA). Lithium perchlorate (Fluka, AG, 99% purity) was dried at 160 °C under vacuum for 24 h.

Apparatus and procedure

A Cannon–Fenske direct-flow viscometer was used for viscosity measurements. It was standardized by measuring the times of flow of conductivity of water, acetone, propylene carbonate and acetonitrile, whose viscosity values are given in ref. 13. The viscometer constant determined through this procedure was $0.000874 \text{ kg m}^{-1} \text{ s}^{-1}$. The kinetic energy term for the viscometer was well within the experimental error and, therefore, neglected. At least three determinations were made for each solution in order to check the reproducibility of the time of flow to within ± 0.2 s. This leads to an error of ± 0.04 to 0.08%. Therefore, the overall uncertainty of the viscosity values is within 0.1%.

Conductivity measurements were performed with a Wayne Kerr autobalance precision bridge (type B 331/MK 11) that had a frequency of 1592 Hz. A conductance cell similar in design to that reported by Schedlovsky [14] was used, with electrodes made from bright platinum discs soldered in glass. The electrode compartment was sealed to the side of a 250 cm^3 conical flask that was closed with a ground-glass cap. The cell was calibrated following the method of Fuoss and co-workers [15]. This involved the use of aqueous potassium chloride solutions in the concentration range 3×10^{-4} to $50 \times 10^{-4} \text{ mol dm}^{-3}$. The cell constant was determined to be 0.3354 cm^{-1} . All experiments were performed inside a glove box in which argon gas was circulated. The temperature inside the glove box was maintained at 25 °C. Taking account of the purity of the electrolyte and solvents and also the experimental procedure, the overall accuracy of the conductance measurements was $\pm 0.1\%$.

Results and discussion

The physical properties of the organic solvents used in the present study are given in Table 1, and their molecular structures are shown in Fig. 1. Variations in the viscosity of the three types of solvent mixtures, without and with the electrolyte

TABLE 1
Physical properties of solvents [5, 6]

Solvent	Dielectric constant, 25 °C	Viscosity $\eta \times 10^{-3}$, 20 °C (kg m ⁻¹ s ⁻¹)	Molecular volume (Å ³)	Donor number	Acceptor number
Dimethyl sulfoxide	46.7	2.0	118.4	29.8	19.3
Tetrahydrofuran	7.6	0.555	134.8	20.0	8.0
1,2-dimethoxyethane	7.2	0.48	172.4	24.0	10.0
1,3-dioxolane	7.0	0.57	116.1	~24.0	

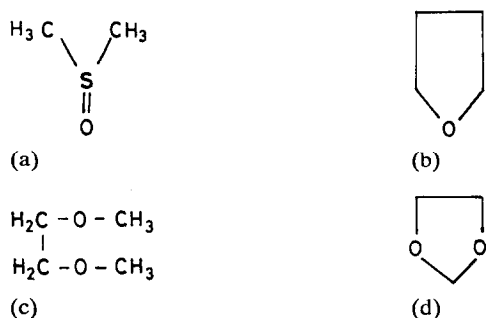


Fig. 1. Molecular structures of solvents: (a) dimethyl sulfoxide; (b) tetrahydrofuran; (c) 1,2-dimethoxyethane, and (d) 1,3-dioxolane.

compound at the four concentrations, are shown in Figs. 2 to 4. The changes in viscosity appear to be similar in all three cases.

As seen in Fig. 2, the viscosity exhibits a continuous increase with increase of the DMSO content in THF. The viscosity-composition curve (without electrolyte) is concave upward and, thereby, displays a slight negative deviation from ideal behaviour. This indicates the existence of interaction between the two components of the mixture. The negative deviation from ideal behaviour is generally attributed to a structure-breaking influence of one component on the other. Pure DMSO possesses intermolecular association through non-specific dipole-dipole forces [16, 17]. The interaction between DMSO and THF is such that the basic network of intermolecular association in DMSO will be disrupted and the individual DMSO and THF molecules will be loosely bound together to give rise to a less-structured solution. A loose association of molecules would give rise to an apparent slight negative deviation in the variation of viscosity. This explanation is also valid for the other two systems because of the observed similarity in the viscosity behaviour. These viscosity variations are analogous to those reported for both ethylene glycol+water [18] and formamide+water mixtures [19].

It can also be observed from Figs. 2 to 4 that the viscosity increases with the addition of electrolyte in all the solvent mixtures at each composition. An increase in concentration from 0.5 and 2.0 M gives an increase in viscosity at each composition of the mixtures. This effect may be attributed to the association of Li⁺ and ClO₄⁻ ions with the solvent molecules that results in the formation of solvated complexes

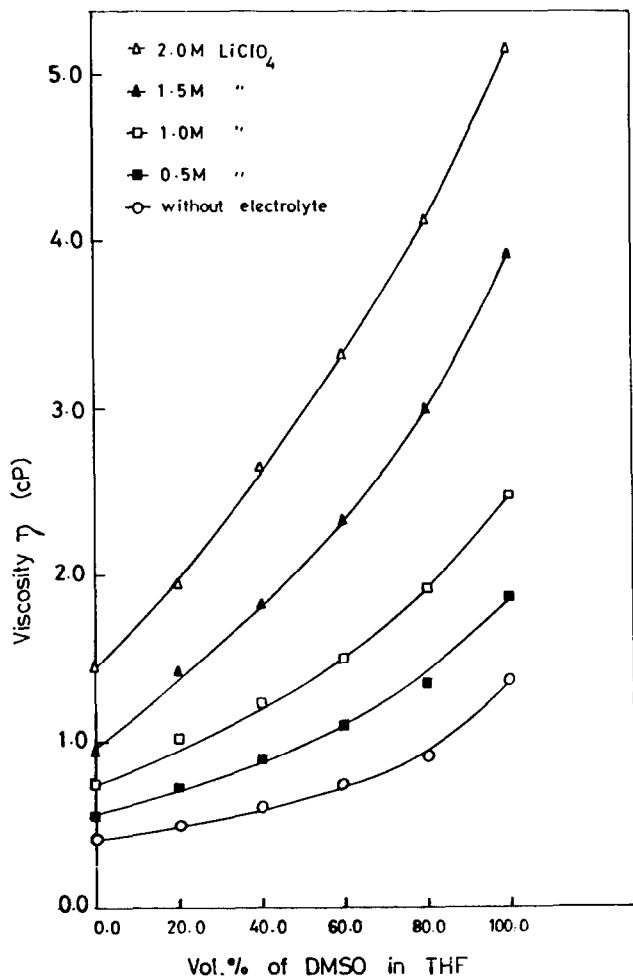


Fig. 2. Viscosity of DMSO + THF mixtures containing LiClO₄ at different concentrations at 25 °C.

(solvent-separated ion-pair) [20]. Evidence for the formation of solvated complexes is also provided by the conductivity results discussed below.

Both the components of the solvent mixtures have the heteroatom 'oxygen' which acts as the complexing centre. When the electrolyte LiClO₄ is added to the solvent mixtures, the dissociated Li⁺ and ClO₄⁻ ions become associated with the individual solvent molecules. As these associated species form, the ions are accommodated in the interstitials (voids) that are available in the mixtures. This contributes to the structural enhancement in the solutions that, in turn, results in an increase in the viscosity. Moreover, the viscosity increases with increase in the concentration of the electrolyte. This indicates that the structure of the electrolyte solution becomes increasingly compact as more and more ions become accommodated in the interstitial vacancies. This argument applies for all the three systems studied here.

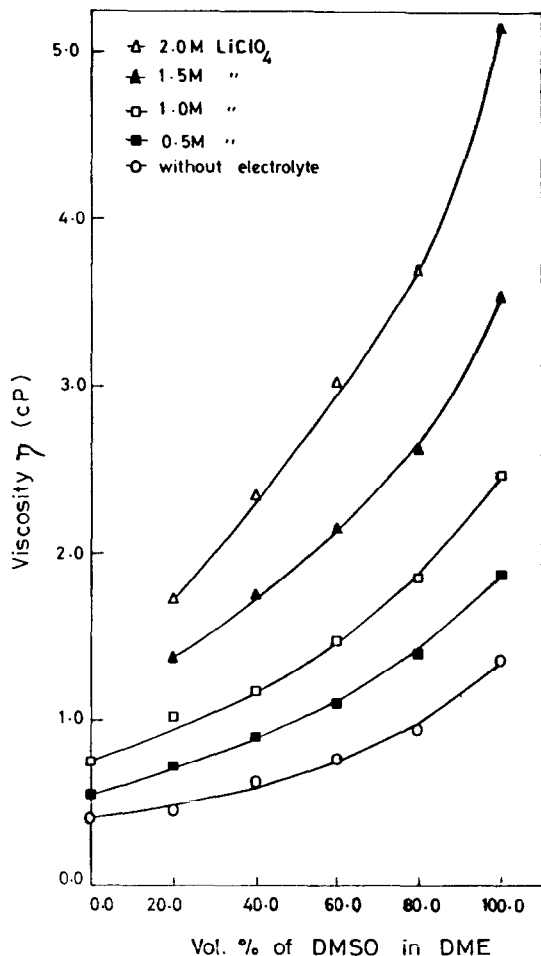


Fig. 3. Viscosity of DMSO + DME mixtures containing LiClO_4 at different concentrations at 25 °C.

The specific conductivity at four different concentrations of the electrolyte (LiClO_4) as a function of solvent composition in the three binary mixtures is presented in Figs. 5 to 7. The specific conductivity for 1 M LiClO_4 in pure DMSO, THF, DME and DOL is 6.15, 4.8, 5.9 and 5.6 mS cm^{-1} , respectively. The reported values [3, 5, 6] for 1 M LiClO_4 in these solvents in the same sequence are 11.5, 4.0, 7.2 and 1.8 mS cm^{-1} , respectively. The reported values are not markedly different from those obtained in this study. Despite the possible unaccounted experimental errors and also the difference in the purification methods adopted, the accuracy of the experimental results presented here is reasonable. It can be seen from the data in Figs. 5 to 7 that the conductivity increases with increase in the DMSO content in the three solvent mixtures, and passes through a maximum at all the four concentrations. A 2 M LiClO_4 solution shows a maximum conductivity at 20 vol.% DMSO in DMSO + DOL and at 40 vol.% DMSO in DMSO + THF mixtures, whereas 1.5 M LiClO_4 solutions shows a maximum

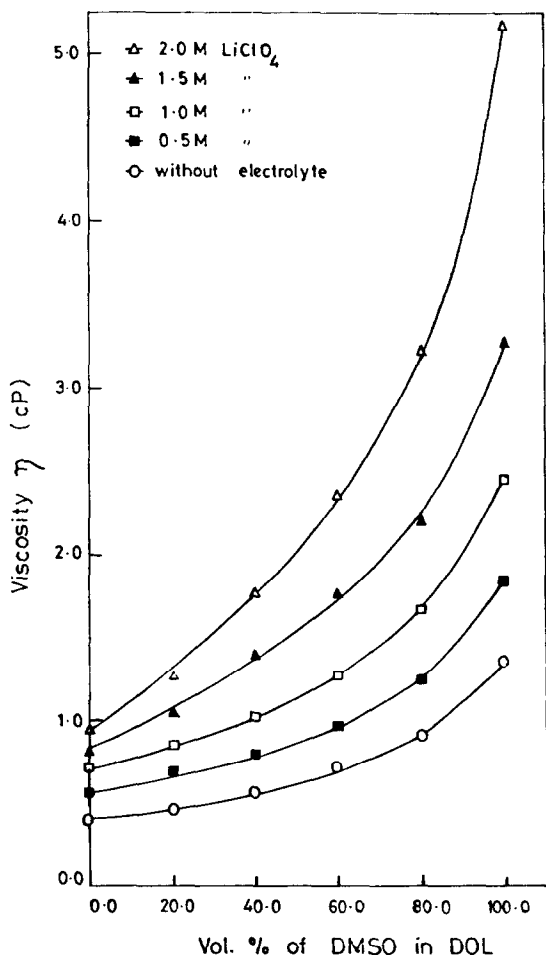


Fig. 4. Viscosity of DMSO + DOL mixtures containing LiClO₄ at different concentrations at 25 °C.

conductivity at 40 vol.% DMSO in DMSO + DME mixtures. These conductivity variations and the appearance of conductivity maximum can be explained qualitatively in terms of a favourable combination of high dielectric solvent DMSO and the low-viscosity co-solvents (viz., THF, DME and DOL). The electrolyte solutions of low-viscosity ethers, which have a low dielectric constant (~ 7.0), contain more contact ion-pairs because of the greater degree of ion association. When an electrolyte solution of high dielectric solvent DMSO is added to the ether solutions, the conductivity increases because of the gradual dissociation of these ion-pairs. Even though the viscosity increases with increase in the DMSO content (see Figs. 2 to 4), the high dielectric constant of DMSO appears to be a greater determinant of the increase in ionic mobility in the co-solvent (THF, DME and DOL)-rich region. After passing through the maximum, the conductivity decreases gradually with further increase in the DMSO content (see Figs. 5 to 7). This may be due to the predominant influence of the viscosity on the mobility of ions in the DMSO-rich region. Therefore, as a first approximation, these

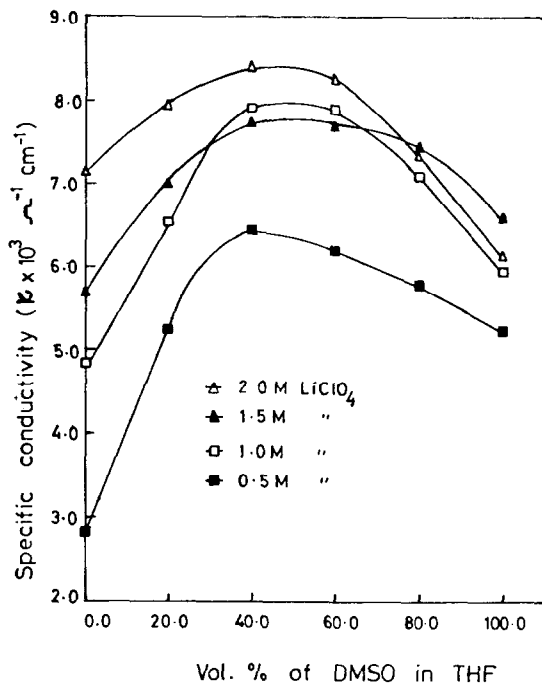


Fig. 5. Specific conductivity of LiClO₄ in DMSO + THF mixtures at different concentrations at 25 °C.

conductivity variations are considered to be a result of the compensation of viscosity and dielectric constant of the solvent components of the mixtures.

Despite the observations reported above, there appears to be appreciable differences in the conductivity variations of the three different electrolyte solutions under study. For example, Fig. 8 shows differences in conductivity at those concentrations where the maximum specific conductivity is observed in each mixture. These differences may be explained on the basis of the following considerations. At high electrolyte concentration and also in solutions of low dielectric constant, essentially two types of ion-pairs exist [20], namely, solvent-separated ion-pairs and solvated-contact ion-pairs. These are represented by the following equilibria:



where S represents a solvent molecule and A⁻ an anion. It is possible that redissociation of solvent-separated ion-pairs occurs because of the long-range nature of the coulombic force and that the resulting free ions contribute to ionic conductance. In other words, the existence of different types of ionic species would give rise to the difference in the ionic behaviour of these solutions. This implies that the degree to which the short-range ion-solvent interactions differ determines the differences in the ionic behaviour in the three electrolyte solutions under examination.

It can also be observed from the data in Figs. 5 to 7 that the conductivity curves intersect at different concentrations of the electrolyte, particularly at 2.0, 1.5 and

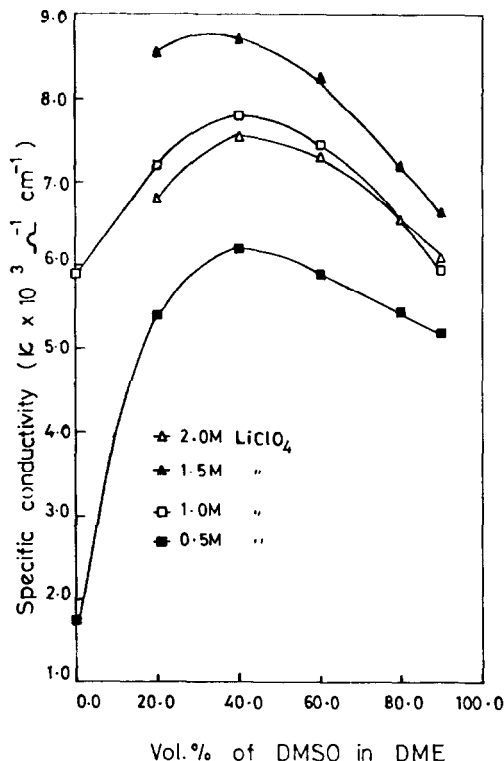


Fig. 6. Specific conductivity of LiClO_4 in DMSO+DME mixtures at different concentrations at 25 °C.

1.0 M. At higher concentrations, the presence of different types of ionic species and the competitive interactions between them may possibly lead to such ambiguous variations. Also, the conductance values for 2 M LiClO_4 in DMSO+DME solutions are less than those obtained for 1.5 M LiClO_4 solutions. It may be noted that 1.5 M LiClO_4 is the optimum concentration where a larger number of free ions are available to contribute to the increase in conductance current compared with those solutions containing a higher electrolyte concentration (e.g., 2 M LiClO_4). The short-range ion-solvent interactions may be partly responsible for the conductance behaviour of the DMSO+DME solutions.

The conductivity variations are, therefore, explained on the basis of differences in the short-range ion-solvent interactions. It can be observed from Fig. 8 that the maximum specific conductivity does not correspond to a particular composition in the three solutions. This suggests the occurrence of preferential solvation of the electrolyte ions (Li^+ and ClO_4^-) by either one of the solvent components of the binary mixtures. This means that the solvation state of the Li^+ ions in the co-solvent (THF, DME or DOL)-rich region is different in the three mixtures. It is possible to explain this phenomenon of preferential solvation on the basis of a donor-acceptor model [21]. The donor number and the acceptor number (DN and AN, respectively) are a measure of the solvation power of the electrolyte ions towards the solvent molecules. This gives an idea about the solvent environment around the electrolyte ions. The DN and AN

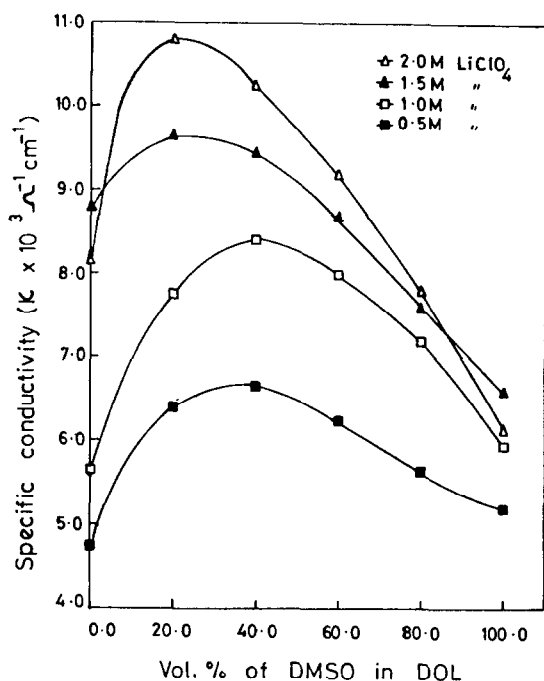


Fig. 7. Specific conductivity of LiClO_4 in DMSO + DOL mixtures at different concentrations at 25 °C.

of the solvents used in the present study are listed in Table 1. The DN and AN of THF (20.0, 8.0) DME (24.0, 10) and DOL (24.0, -) are considerably lower than those of DMSO (19.0, 19.3). Therefore, the Li^+ and ClO_4^- ions are expected to be preferentially solvated by DMSO in the binary mixtures with THF, DME and DOL, respectively. It is not clear from the conductivity variations, however, that DMSO causes preferential solvation of the Li^+ ions.

It can be observed from Fig. 8 that the conductance values of the three electrolyte solutions varies in the following order in the co-solvent-rich region (up to 50 vol.% DMSO): DMSO + DOL > DMSO + DME > DMSO + THF. In the DMSO-rich region, the trend of decrease in conductance is approximately the same and there exists little difference in the conductance values of the three solutions. It is clear from these observations that the extent of preferential solvation depends on the solvent composition. The observed order of variation of conductance in the co-solvent-rich region can possibly be explained by taking the molecular volumes of the solvent components into account. Initially, the primary solvation shell around the Li^+ and ClO_4^- ions contains more co-solvent molecules (THF, DME or DOL).

A gradual increase in the DMSO content in the mixtures results in a gradual replacement of co-solvent molecules in the vicinity of the Li^+ ions by DMSO molecules. This is due to the relative differences in the affinity of the electrolyte ions towards DMSO (refer to DN values). In the case of binary mixtures with DME and THF, the solvated Li^+ ion is larger in size (in co-solvent-rich region) because of the higher molecular volumes of DME (172.4 Å) and THF (13.48 Å) compared with that of DMSO (118.4 Å). In view of these differences in molecular volumes, the replacement

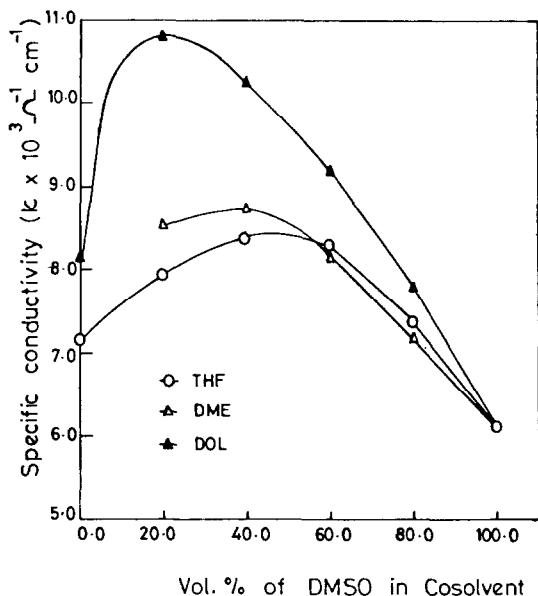


Fig. 8. Specific conductivities for 2 M LiClO_4 in DMSO+DOL and DMSO+THF mixtures, and 1.5 M LiClO_4 in DMSO+DME mixtures.

of DME and THF molecules (in their respective binary mixtures with DMSO) by DMSO molecules may be expected to occur slowly. This may be the reason for the lowering of the conductivity of these solutions. Also, there is not much difference in the molecular volumes of DME and THF, the mechanism of the replacement process in these two solutions appears to be similar. This results in only a small difference between the conductance values of these two solutions in the co-solvent-rich region (see Fig. 8).

In DMSO+DOL solutions, the conductance is higher compared with the other two binary systems. The molecular volumes of DMSO (118.4 Å) and DOL (116.1 Å) are approximately the same. This leads to an easy replacement of DOL molecules in the primary solvation shell by DMSO molecules. This accounts for the significant increase in the conductivity of DMSO+DOL solutions in the co-solvent-rich region. Thus, the order of conductance variations observed in the co-solvent-rich region of the three different solutions is explained.

In the DMSO-rich region, the DMSO molecules may exert a dominating influence over the co-solvent molecules (THF, DME and DOL) with respect to the solvation mechanism. This results in a more or less similar trend in the decrease of the conductance of the three solutions.

Further, the Walden product variations give an insight into the short-range ion-solvent interactions. In general, for electrolyte solutions of low concentration ($\sim 1 \times 10^{-3}$ M) variations in the Walden product can be interpreted meaningfully. At infinite dilution, long-range ion-ion interactions are completely absent and ion-solvent interactions alone are taken into consideration. Therefore, Walden product variations are effectively interpreted on the basis of short-range ion-solvent interactions.

In the present study, however, Walden product values are determined at high electrolyte concentration (~ 2 M). In such solutions, ion-ion and ion-solvent interactions

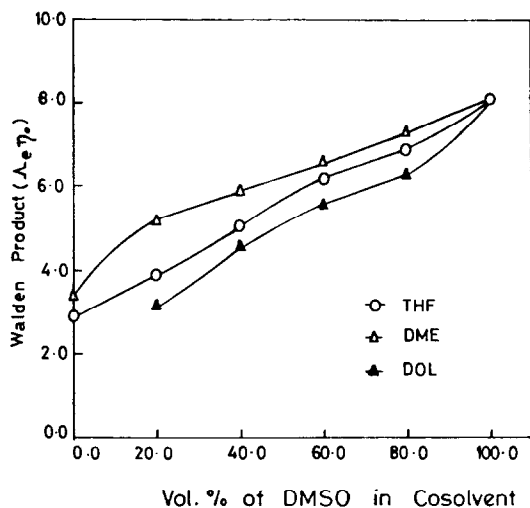


Fig. 9. Walden product for 2 M LiClO_4 in DMSO+DOL and DMSO+THF mixtures, and 1.5 M LiClO_4 in DMSO+DME mixtures.

exist. Consequently, these solutions have solvent-separated ion-pairs, solvated-contact-pairs, contact-pairs and also free ions that contribute to the conductance current. The differences in the Walden product variations represent the degree of ionic behaviour that arises from the presence of different types of ionic species in the three solutions.

The variations of Walden product with respect to solvent composition are shown in Fig. 9. In the three cases, the Walden product values increase as the DMSO content increases in the solvent mixtures. The trend of variation in Walden product is not very different in the three mixtures. At any particular composition of these mixtures, the order of variation in the Walden product is as follows: DMSO + DOL > DMSO + THF > DMSO + DME. This behaviour can be attributed to the extent of availability of free ions that contribute to the increase in conductivity. The observed order indicates that the polarizability of DMSO + DOL solutions is higher and gives rise to relatively more free ions compared with the other two systems. Apparently, DMSO + DME solutions have less conductivity due to the relatively poor polarizability in these solutions. The Walden product variations of DMSO + THF solutions fall between those of DMSO + DOL and DMSO + DME. This illustrates the relative differences in polarizability of DMSO + THF solutions from the other two systems.

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