Viscosity *B*-Coefficients for Lithium Perchlorate in Ethylene Glycol-Water Mixtures

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Viscosities and densities of lithium perchlorate solutions in different ethylene glycol-water compositions have been measured at 25.0 and 35.0 °C. From these data, the corresponding *B*-coefficients of the *Jones-Dole* equation have been determined. The *B*-value depends on the solvent composition and it reaches a maximum in the water-rich region. This behaviour is analysed in terms of ionic solvation and solvent structure.

(Keywords: B-Coefficient; Lithium perchlorate; Ethylene glycol mixtures)

Viskositäts-B-Koeffizienten für Lösungen von Lithiumperchlorat in Ethylenglykol-Wasser-Mischungen

Es wurden die Dichten und Viskositäten für Lösungen von Lithiumperchlorat in verschieden zusammengesetzten Ethylenglykol-Wasser-Mischungen bei 25 °C und 35 °C gemessen. Auf Grund der erhaltenen Daten wurden die *B*-Koeffizienten in den entsprechenden *Jones-Dole*-Gleichungen für die relative Viskosität bestimmt. Die *B*-Werte hängen von der Zusammensetzung des Lösungsmittels ab und erreichen im wasserreichen Konzentrationsgebiet ein Maximum. Dieses Verhalten wird in Hinblick auf die Ionensolvatation und die Struktur des Lösungsmittels analysiert.

Introduction

The properties of ethylene glycol (*EG*)-water mixtures have been object of numerous works concerning basically their acid-base behaviour. In these studies, however, there is a certain controversy about the structure of these mixtures. Thus, some authors assume a decrease in

solvent structure when *EG* is added to water-rich compositions [1-6], whereas others conclude that the opposite is true, i.e., an increase in solvent structure in this range of solvent compositions [7-9].

The study of the solvent structure can be carried out by means of an analysis of the viscosity data. The relative viscosity, η_r, of a dilute electrolyte solution can be related to the salt concentration, c, according to the *Jones-Dole* equation [10]:

$$\eta_r = 1 + A c^{\frac{1}{2}} + B c$$

where A and B are two constants. The A-coefficient depends on ion-ion interactions and its value can be determined theoretically [11]. The B-value gives an indication of the order or disorder introduced by the ions in the solvent structure, that is, the ions can be classified by their tendency to change the solvent structure, according to the B-dependence with the temperature [12]; ions whose B-coefficients decrease with temperature are "structure-making", whereas those showing the opposite effect are "structure-breaking". It is apparent that the B-value, together with its temperature dependence, varies with solvent nature, thus providing an interesting method for ascertaining the solvent structure [12, 13].

In the present paper, viscosities and densities of lithium perchlorate solutions in several *EG*-water mixtures have been measured at 25.0 and 35.0 °C. From these data the corresponding B-coefficients have been determined, being analysed in terms of ionic solvation and solvent structure.

Experimental

The experimental techniques and procedures for the measurements of viscosities and densities of electrolyte solutions have been previously described in detail [14].

Ethylene glycol (Fluka, A.R. grade) was dried over molecular sieves (3 Å); the water content determined by the *Fischer* method was lower than 0.05%. Lithium perchlorate (Fluka, A.R. grade) was dried at 130 °C under reduced pressure and kept dry afterwards. All the mixtures and electrolyte solutions were prepared by weight with water obtained using a Millipore Milli Q system.

Results and Discussion

The densities and relative viscosities for lithium perchlorate solutions were measured within a concentration range from 0.006 to 0.1 M in pure *EG* and *EG*-water mixtures of different compositions at 25.0 and 35.0 °C. Results are reported in Table 1. It must be noted that the absolute viscosities for pure *EG* and *EG*-water mixtures in the absence of LiClO$_4$ were also determined and the values thus obtained were in accordance with those reported by *Accascina* et al. [15].

Table 1. *Densities and relative viscosities of* $LiClO_4$ *solutions in EG-water mixtures at 25.0 °C and 35.0 °C*

25.0 °C			35.0 °C		
$c/mol \cdot dm^{-3}$	$d/g \cdot cm^{-3}$	η_r	$c/mol \cdot dm^{-3}$	$d/g \cdot cm^{-3}$	η_r
$X_{H_2O} = 0.899$					
0.00714	1.0335	1.0008	0.00711	1.0309	1.0011
0.01559	1.0342	1.0018	0.01552	1.0316	1.0024
0.03056	1.0354	1.0035	0.03042	1.0327	1.0045
0.05151	1.0368	1.0059	0.05118	1.0342	1.0078
0.07104	1.0384	1.0081	0.07049	1.0357	1.0109
0.10000	1.0403	1.0114	0.09911	1.0378	1.0153
$X_{H_2O} = 0.803$					
0.00663	1.0584	1.0007	0.00660	1.0537	1.0009
0.01304	1.0588	1.0014	0.01297	1.0541	1.0018
0.02561	1.0596	1.0028	0.02547	1.0550	1.0036
0.04594	1.0610	1.0047	0.04575	1.0563	1.0063
0.05586	1.0617	1.0058	0.05562	1.0570	1.0077
0.06492	1.0622	1.0066	0.06466	1.0576	1.0086
$X_{H_2O} = 0.700$					
0.00683	1.0756	1.0006	0.00678	1.0688	1.0008
0.01395	1.0759	1.0013	0.01387	1.0692	1.0017
0.02697	1.0765	1.0023	0.02683	1.0698	1.0032
0.04855	1.0776	1.0043	0.04827	1.0708	1.0059
0.06717	1.0784	1.0058	0.06679	1.0717	1.0080
0.09459	1.0798	1.0082			
$X_{H_2O} = 0.404$					
0.00781	1.0983	1.0003	0.00799	1.0912	1.0004
0.01440	1.0989	1.0007	0.01758	1.0919	1.0009
0.03290	1.0997	1.0014	0.03145	1.0927	1.0015
0.05406	1.1008	1.0023	0.05676	1.0935	1.0028
0.07046	1.1025	1.0032	0.07752	1.0947	1.0038
0.09043	1.1030	1.0039	0.09745	1.0954	1.0047
$X_{H_2O} = 0.000$					
0.00819	1.1109	1.0004	0.00814	1.1044	1.0004
0.01473	1.1114	1.0006	0.01387	1.1047	1.0007
0.02682	1.1121	1.0010	0.02759	1.1051	1.0013
0.04626	1.1134	1.0018	0.05849	1.1070	1.0024
0.07167	1.1150	1.0025	0.07120	1.1074	1.0029
0.10070	1.1163	1.0036	0.10010	1.1085	1.0041

From the data of Table 1, the *A*- and *B*-coefficients of the *Jones-Dole* equation for $LiClO_4$ were determined by fitting $(\eta_r - 1)\,c^{-\frac{1}{2}}$ vs. $c^{\frac{1}{2}}$ by the least-squares method. The *A*-coefficient does not vary with solvent composition and temperature, taking a mean value of $1 \cdot 10^{-3}\,dm^{3/2} \cdot mol^{-\frac{1}{2}}$. Values of the *B*-coefficient and its standard deviation at the studied solvent compositions (at 25.0 and 35.0 °C) are summarized in Table 2.

As can be seen from Table 2, decreasing the water content in the solvent decreases the *B*-coefficient gradually, except in the water-rich region where the *B*-coefficient initially increases when *EG* is added reaching a maximum value at a water mole fraction close to 0.9. This

Table 2. *Viscosity B-coefficients for* $LiClO_4$ *in different EG-water mixtures, at 25.0 and 35.0 °C*

X_{H_2O}	$B/dm^3 \cdot mol^{-1}$	
	25.0 °C	35.0 °C
1 [a]	0.089	0.10
0.899	0.114 ± 0.001	0.154 ± 0.002
0.803	0.100 ± 0.002	0.134 ± 0.003
0.700	0.086 ± 0.002	0.119 ± 0.004
0.404	0.038 ± 0.003	0.048 ± 0.001
0.000	0.032 ± 0.002	0.034 ± 0.001

[a] Data from Ref. [16]

behaviour is shown in Fig. 1, where the dependence of the *B*-coefficient on the solvent composition at 25.0 and 35.0 °C is represented. The low *B*-value obtained in the different solvent mixtures indicates that, in all cases, the solvent is highly structured. The *B*-coefficient found for $LiClO_4$ in pure *EG* is similar to the *KI* in the same solvent, $B = 0.327\,dm^3 \cdot mol^{-1}$ [17]. The presence of two —OH groups in the *EG* molecules favours the formation of intramolecular hydrogen bonds leading to a three-dimensional network. Furthermore, the gradual decrease in the *B*-coefficient as the *EG* content in the solvent increases, can be explained taking into account that the ions become less solvated due to the poor solvating power of the *EG* [2, 3, 7, 18, 19].

The initial increase in the *B*-coefficient when *EG* is added implies the existence of specific interactions between the ion and solvent molecules. In fact, it has been shown [1] that the basicity of the mixtures increases when the *EG* content increases, reaching a maximum for a mole fraction of approximately 0.4 for water. This basicity increase is a consequence of an
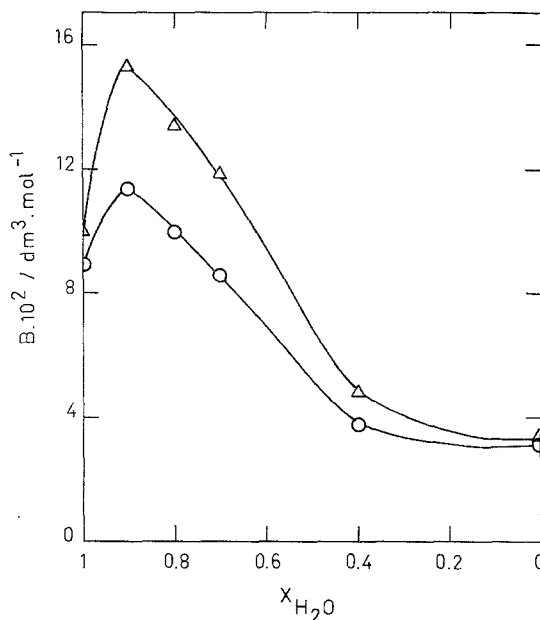
Fig. 1. Viscosity *B*-coefficient for LiClO₄ as a function of solvent composition at 25.0 °C (○) and 35.0 °C (△)

increase of charge density on the negative end of the water dipoles due to the formation of hydrogen bonds with the *EG* molecules. So, some kind of specific acid-base interactions between Li^+ ion (with acid character) and water molecules can be assumed. This leads to stronger interactions between the Li^+ ion and water molecules in the mixtures compared to pure water. This behaviour agrees with the negative ΔG-values of transfer from water to *EG*-water mixtures for alkali ions [19].

Finally, it is interesting to analyse the dependence of the *B*-value from the temperature. Usually, the *B*-coefficient for an inorganic ion is characterised by three contributions: a positive contribution due to the size and shape of the ion, another one which arises from the long-range orientation of solvent molecules around the ion, which is also positive, and a negative contribution due to the breaking of solvent structure produced by the ion. The first contribution is temperature independent, whereas the others show a dependence with temperature [12]. Ions which are markedly "structure-breaking" exhibit positive dB/dT-values, whereas those with "structure-making" characters have negative dB/dT-values. In the present case, the *B*-coefficient for LiClO₄ increases with temperature in all solvent mixtures (Fig. 1). This is not surprising because the solvent

mixtures are highly structured. Moreover, it is apparent that the increase in the *B*-value with temperature is more pronounced in the water-rich region than in pure water; therefore it can be assumed that in this region the solvent becomes more structured than water. A higher content of *EG* in the solvent produces a lower structured solvent because the absolute dB/dT-value decreases (see Fig. 1).

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