

# Volumetric behavior of a bolaamphiphile in different amides–water and ethylene glycol–water mixtures

Fryni Aroni, Antonis Kellarakis, Vasiliki Havredaki \*

*Physical Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, 157 71 Athens, Greece*

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## Abstract

The effect of binary aqueous mixtures of ethylene glycol (EG), formamide (FA), *N*-methylformamide (NMF), dimethylformamide (DMF), and their pure phase on the apparent molar volume  $\phi_V$  of the bolaamphiphile decamethonium bromide ( $C_{10}Me_6$ ) has been investigated at 298.15 K. The behavior of standard molar volumes  $V_2^0$  and transfer volumes  $\Delta_t\phi_V$  of  $C_{10}Me_6$  from water to solvent/water (S/W) binary mixtures, shows different minima and maxima depending on the composition of the solvent. This behavior is influenced by the nature of the cosolvent and on the type of the solute and more or less corresponds to volumetric changes in the S/W mixture. The investigation of the transfer volumes in different fixed concentrations reveals an inversion of  $\Delta_t\phi_V$  values between the compositions, which suggests a differentiation of the effects of different volume contributions on the partial molar volume of ions. The correlation of  $\Delta_t\phi_V$  with the dielectric constant of the aqueous amide mixtures shows that the behavior of  $\Delta_t\phi_V$  vs  $x_{amide}$  reflects the changes of  $\epsilon^E$  vs  $x_{amide}$ .  
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## 1. Introduction

The volumetric behavior of electrolytes in solution can provide information regarding ion–solvent and ion–ion interactions. Of particular relevance is the behavior of surfactant molecules in solvents having different structural properties and even more important but less well known is the way they influence the structure and the properties of mixed solvents. Several attempts have been made to connect this behavior with different properties of the medium and/or the solute shape, size, and charge but such a connection is not yet clarified.

Mixed aqueous solvents have particular interest in chemical, biological, and pharmaceutical applications. Among the different solvents, ethylene glycol (EG) and amides, specially formamide (FA), *N*-methylformamide (NMF), and

dimethylformamide (DMF) have an important position in the study of biological systems. Aqueous solutions of amides contain peptide linkages and are used for modeling biological membranes.

It is well known that water (W) is an excellent solvent having high dielectric constant ( $\epsilon = 78.3$  at 298.15 K). The structure of liquid water consists of clusters wherein the water molecules bond with strong hydrogen bonds forming a three-dimensional array [1,2]. Ethylene glycol is a widely used solvent possessing two –OH, and thus having the possibility of forming hydrogen bonds between the ethylene glycol molecules that are stronger than the monohydroxy alcohols. Its dielectric constant is  $\epsilon = 40.61$  at 298.15 K, reaching higher values in aqueous mixtures of low concentrations in EG. The addition of small amounts of EG in water reinforces the intermolecular interactions between the different solvents molecules (EG–W) [1,3a]. Formamide is the simpler amide possessing three hydrogen-bond donors and three acceptors in the molecule, also forming a three-dimensional hydrogen bond network in the pure

\* Corresponding author.

E-mail address: [vhavre@chem.uoa.gr](mailto:vhavre@chem.uoa.gr) (V. Havredaki).

phase. NMF, the monomethylated formamide, is a protic dipolar solvent possessing the donor (–CO) and acceptor (–NH) groups of amides, thus forming a linear hydrogen-bonded structure. DMF is an aprotic polar solvent. As the two hydrogen atoms of the amide group are substituted by –CH<sub>3</sub>, DMF does not possess hydrogen bonding but dipole–dipole interactions. The two amides possessing hydrogen bonds (NMF, FA) in their pure phase have high dielectric constants ( $\epsilon = 182.4$  and  $109.5$ , respectively) while in the dipolar DMF is quite low ( $\epsilon = 36.71$ ) at  $298.15$  K [3b]. Amides are less structured solvents than alcohols and obviously of water but in aqueous mixtures they form 2D or 3D clusters [4] and show a more compact structure than their pure phases [5].

Decamethonium bromide (C<sub>10</sub>Me<sub>6</sub>) is a dicationic surfactant possessing two positive trimethylammonium groups at the end of the decylhydrocarbon chain. Interest in this kind of substance is both theoretical and practical, especially in biology, as the molecule resembles those forming the biological membranes [6,7]. C<sub>10</sub>Me<sub>6</sub> has already been studied for its the interfacial properties [8] and volumetric and hydrotropic behavior in aqueous solutions [9,10]. C<sub>10</sub>Me<sub>6</sub> has a limited position between the bolaamphiphile (or bolaform) molecules that form micelles, as more than 12-methylene groups in a bolaform alkyl chain are required for micellization to occur. Even in C<sub>12</sub>Me<sub>6</sub> solutions, studied by means of different methods, Zana and co-workers do not prove micellization except a very loose aggregation with a small number of monomers [11]. Therefore, it would be of special interest to investigate the modifications that the aqueous mixed solvents of EG, FA, NMF, and DMF induce in the volumetric behavior of C<sub>10</sub>Me<sub>6</sub> and thus of the symmetrical divalent hydrophobic electrolytes. More over the above-noted amides have a wide range of dielectric constants, higher (FA, NMF) and lower (DMF) than those of water, offering from this point of view, another insight into the investigation.

## 2. Experimental

Decamethonium bromide or decamethylene-bis-trimethylammonium bromide (C<sub>10</sub>Me<sub>6</sub>) was supplied by Sigma–Aldrich (stated purity >99%, water content <0.05%) and dried before use. The solvents were supplied: formamide (stated purity >99%–microselect for molecular biology), *N*-methylformamide (stated purity >99%), and dimethylformamide (stated purity >99.8%) by Fluka and ethylene glycol (stated purity >99.9%) by Acros Organics, and were used without other purification. The water was deionized and distilled prior to use for making up solutions or calibrations. Its specific conductivity at  $25$  °C was  $0.7 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ . Densities were measured with a vibrating tube digital densimeter (A. Paar, DMA 58) with a resolution of  $10^{-6} \text{g cm}^{-3}$ . The precision of density reading was within  $5 \times 10^{-6} \text{g cm}^{-3}$ , the accuracy was  $3 \times 10^{-5} \text{g cm}^{-3}$ , and the temperature was kept constant within  $0.01$  K by an

Table 1  
Densities of pure solvents  $\rho$  ( $\text{g cm}^{-3}$ ) at  $298.15$  K

W	FA	NMF	DMF	EG
0.99704 <sup>a</sup>	1.12901 <sup>a</sup>	0.99876 <sup>a</sup>	0.94404 <sup>a</sup>	1.10737 <sup>a</sup>
0.997047 <sup>b</sup>	1.12975 <sup>c</sup>	0.99929 <sup>c</sup>	0.94406 <sup>c</sup>	1.1086 <sup>d</sup>
0.99705 <sup>c</sup>	1.129155 <sup>e</sup>	0.99889 <sup>f</sup>	0.94559 <sup>g</sup>	1.109913 <sup>g</sup>
			0.942915 <sup>h</sup>	

<sup>a</sup> This work.

<sup>b</sup> Ref. [12a].

<sup>c</sup> Ref. [5].

<sup>d</sup> Ref. [12b].

<sup>e</sup> Ref. [12c].

<sup>f</sup> Ref. [12d].

<sup>g</sup> Ref. [12e].

<sup>h</sup> Ref. [12f].

internal Peltier element of the apparatus. The apparatus cell was calibrated with dry air and distilled water at the beginning of every set of experiments. Densities of pure water and solvents were compared with the values obtained in the literature to confirm their purity and temperature constancy (Table 1).

All binary aqueous mixtures (W/solvent) were prepared by mass covering the whole region from 0 to 100% in solvent: EG (0, 10, 25, 50, 65.2, 75.2, 90, and 100%), FA (0, 10, 25, 50.6, 74.5, 95.1, and 100%), NMF (0, 10, 25.1, 50, 60, 75, 79.8, 92.8, and 100%), and DMF (0, 25.3, 35.2, 46.4, 50, 62.4, 75.5, 84.8, 95.1, and 100%). The solutions of C<sub>10</sub>Me<sub>6</sub> were all made by mass in the binary aqueous solvent.

## 3. Results and discussion

Apparent molar volumes  $\phi_V$  for C<sub>10</sub>Me<sub>6</sub> at different concentrations have been calculated from solution densities by the equation,

$$\phi_V = \frac{M_2}{\rho} + \frac{1000(\rho_0 - \rho)}{m\rho\rho_0}, \quad (1)$$

where  $M_2$  is the molar mass ( $\text{g mol}^{-1}$ ) of the bolaamphiphile,  $\rho$  and  $\rho_0$  the density of the solution and solvent ( $\text{g cm}^{-3}$ ), respectively, and  $m$  the mean molality (number of moles of solute per kilogram of mixed solvent).

According to the Mason equation [13,14]

$$\phi_V = \phi_V^0 + S_V^* c^{1/2} \quad (2)$$

applied to electrolytic solutions of low concentration, extrapolation to zero concentration ( $c$  or  $m \rightarrow 0$ ) provides the apparent molar volume at infinite dilution  $\phi_V^0$ , where  $S_V^*$  is the experimental slope for given temperature and pressure that varies with solvent and solute. The  $\phi_V^0$  equals the partial molar volume of solute at infinite dilution, called standard partial molar volume  $V_2^0$ ,

$$\lim_{c \rightarrow 0} \phi_V = \phi_V^0 = V_2^0. \quad (3)$$

If the Debye–Hückel limiting law (DHLL) is obeyed, a constant limiting slope  $S_V$  is obtained, depending only, for

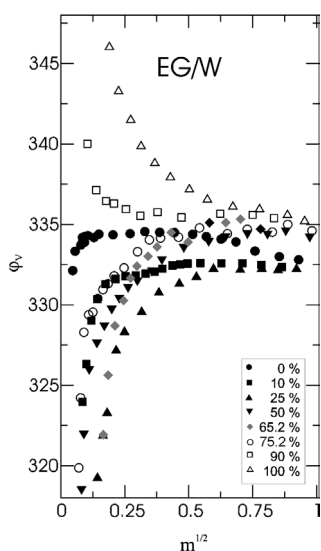


Fig. 1. Apparent molar volumes of  $C_{10}Me_6$  in EG/W solutions at 298.15 K.

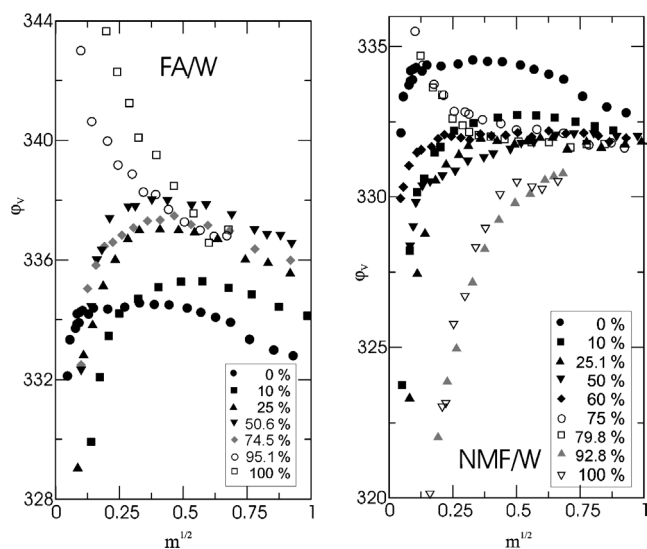


Fig. 2. Apparent molar volumes of  $C_{10}Me_6$  in FA/W and NMF/W solutions at 298.15 K.

given temperature and pressure, on the electrolyte charge type and the solvent used as Redlich and Rosenfeld predicted, analogous to the Mason equation, where  $S_V$  is theoretically computed [13,14]. The theoretical value of  $S_V$  for 2:1 electrolytes in low concentration aqueous solutions is 9.706 at 25 °C and it was fitted to data of many divalent electrolytes in low concentration aqueous solutions [14,15]. The application of the Redlich equation is not possible for most solvents due to the lack of values of the theoretical limiting slopes  $S_V$  as in the case of our solvent mixtures.

The apparent molar volumes  $\phi_V$  are plotted against  $m^{1/2}$  for  $C_{10}Me_6$  in solvent/water mixtures as well as in aqueous solutions, in order to compare the behavior progressively reached from pure water to pure solvent via different water–solvent mixtures (Figs. 1–3). Some of the  $\phi_V$  values for very low concentrations of  $C_{10}Me_6$  are not included in the fig-

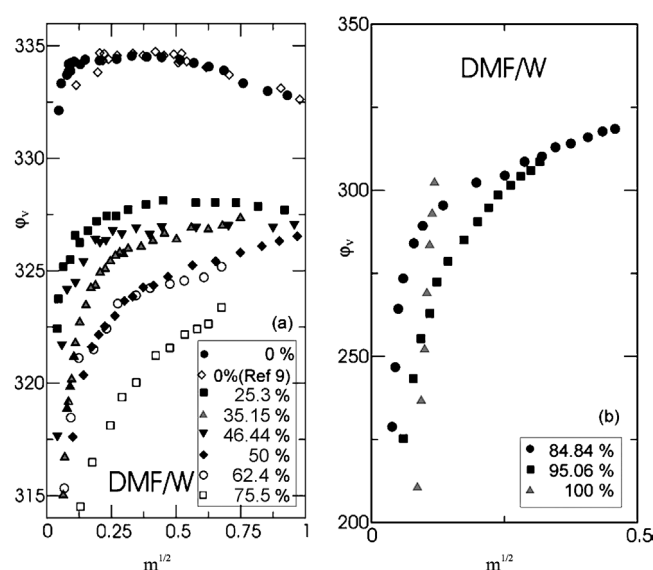


Fig. 3. Apparent molar volumes of  $C_{10}Me_6$  in DMF/W solutions at 298.15 K.

ures as the scale in the axes is decreased and differences of plots are not visible. The behavior of  $C_{10}Me_6$  in aqueous solution, although studied by Johnson and Fleming [9], is also included in our experiments for a better and more realistic comparative study. The  $\phi_V$  measurements in aqueous solutions were repeated two times from different preparations of the initial concentrations because of the importance of the  $\phi_V$  of aqueous solutions as reference solutions. The  $\phi_V = f(m^{1/2})$  plot was in good agreement with the Johnson and Fleming plot, specially in medium and high concentrations, but the DHLL applied to our data in low concentrations (0.01–0.035  $m$ ) gives for  $C_{10}Me_6$  in aqueous solutions,  $\phi_V^0 = 333.5 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$ , compared to the value of  $332.4 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$  that results from the Johnson and Fleming plot [9] and the value of  $334.4 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$  proposed by Zana and co-workers [11]. In Fig. 3a, we have included the plot obtained by Johnson and Fleming [9]. Their points were read directly from the graph, while the concentration (expressed in mol/L) has been converted to molality according to our experimental relation of  $m = f(c)$ .

In a recent review paper Marcus and Hefter [16] as well as Millero [15] in a previous review and other authors [10, 17,18] discuss and point out the significance of the precise density measurements in dilute solutions where considerable scattering is observed and of the limits of low concentration regions for accurate  $S_V$  slopes. In the low concentration range, the extrapolation of the  $\phi_V = f(m^{1/2})$  curve gave the apparent molar volume of  $C_{10}Me_6$  at infinite dilution  $\phi_V^0$  (and so the standard molar volume  $V_2^0$ ) for all the compositions of mixed solvents expressed in mole fractions of the cosolvent (Table 2). The uncertainties of  $\phi_V^0$  in most cases are  $\sim \pm 2 \text{ cm}^3 \text{ mol}^{-1}$  and often lower except in the high compositions of DMF where they are greater and the  $\phi_V^0$  values are estimated just for indication of the trends of  $\phi_V^0$  change.

Table 2

Apparent molar volumes at infinite dilution  $\phi_V^0$  ( $\text{cm}^3 \text{mol}^{-1}$ ) of  $\text{C}_{10}\text{Me}_6$  in water, pure solvent, and solvent/water mixtures of different compositions, at 298.15 K

FA		NMF		DMF		EG	
$x$	$\phi_V^0$	$x$	$\phi_V^0$	$x$	$\phi_V^0$	$x$	$\phi_V^0$
0	333.5	0	333.5	0	333.5	0	333.5
0.0425	323.5	0.0328	323	0.0770	321	0.0312	315
0.1174	330.5	0.0927	317.5	0.1179	311.5	0.0884	306
0.2908	332	0.2336	323	0.1761	317	0.2252	318
0.5448	332.5	0.3136	328	0.1978	313	0.4685	324
0.8860	346.0	0.4775	344	0.2895	313.5	0.7230	343
1	351.0	0.5459	346.5	0.4311	309	1	355
		0.7969	312	0.5798	<200		
		1	313	0.8260			
				1			

All the  $\phi_V$  curves of  $\text{C}_{10}\text{Me}_6$  in different FA/W compositions lay over those of the aqueous solutions while those of NMF/W and DMF/W are under that curve. In the case of EG/W, the water-rich compositions are below the  $\phi_V$  curve of  $\text{C}_{10}\text{Me}_6$  in aqueous solution while the curves of cosolvent-rich compositions lay above it. Furthermore, it is worth noting, especially in the case of EG/W and FA/W solutions, the sequence that the  $\phi_V$  curves are superimposed in the different solvent/W compositions. Positive  $S_V^*$  slopes are observed in all EG, FA, NMF, and DMF solutions except at compositions over 90% in EG and FA and within 70–85% in NMF, where  $S_V^*$  is negative. In pure FA, the DHLL slope  $S_V$  at 298.15 K is 1.104 calculated by Dunn [19] from experimentally determined  $\partial \ln \varepsilon / \partial P$  data ( $\varepsilon$ , dielectric constant;  $P$ , pressure) according to the Redlich equation. However negative  $S_V^*$  has been found for a number of electrolytes in FA and in different other solvents [18,20–23] as well as in aqueous solutions. Going from higher to lower compositions, there is a change in the sequence of  $\phi_V$  curves, after 25% in EG/W and after 75% in FA/W. For confirmation, the measurements in several compositions were repeated. In high solvent compositions, the greater solution concentration measured is progressively lower due to the diminished solubility of  $\text{C}_{10}\text{Me}_6$  and specially in high DMF compositions.

In concentrations higher than 0.16 M ( $\sim 0.16m$ ), the  $\phi_V$  values of  $\text{C}_{10}\text{Me}_6$  in aqueous solutions decrease [9] as well as  $\phi_V$  of  $\text{C}_{12}\text{Me}_6$  in aqueous solutions [11]. This decrease and the great deviations from DHLL in aqueous solutions of  $\text{C}_{10}\text{Me}_6$  were attributed to the curved configuration of the bolaform molecules even inside the solution [8,9], although later this bending was not detectable in  $\text{C}_{12}\text{Me}_6$  by relaxation methods [11]. Similar behavior is observed in plots of our data in high solute concentrations of the hydrogen-bonded cosolvents (all FA compositions, 10% NMF and 10% EG) while contrary to the aprotic DMF,  $\phi_V$  increases with continuously higher slope as the solvent becomes more rich in DMF. As the solute is the same in all cases, this concentration dependence must be influenced by the nature

of the solvent and may be due mostly to cation–cation interactions, giving rise somewhat to the association of hydrophobic species, although there is no sharp transition of the  $\phi_V$  indicative of micellization. Nevertheless, the hydrophilic character of all FA/W and low EG/W, NMF/W compositions obviously influence the volumetric behavior of the hydrophobic solute (this will be more clearly shown later in discussions on the transfer volume of the solute). In all these cases, except 90% and pure EG, 95.1% and pure FA, 75 and 79.8% NMF, there is an increase in  $\phi_V$  before reaching constant or slightly decreasing values in high concentrations.

The volumetric behavior of the solvent/water mixture itself in the absence of solute ions should be known for the detection of the effect of a mixed solvent on the volumetric behavior of  $\text{C}_{10}\text{Me}_6$ . This was investigated with experiments done in our laboratory and also with data found in the literature. The  $\phi_V = f(x_{\text{sol}})$  plot, where  $x_{\text{sol}}$  is the mole fraction of the cosolvent, is indicative of the cosolvent–water interactions. The plot  $\phi_V = f(x_{\text{sol}})$  of FA/W [5,24] shows a continuous increase of  $\phi_V$ , where the gradient  $d\phi_V/dx$  of the plot is slightly changed at  $x = \sim 0.32$  (54%). The  $\phi_V = f(x_{\text{sol}})$  plots of DMF/W [5,25] and EG/W [12b] show a minimum at  $x = \sim 0.12$  (35.6%) and  $x = \sim 0.1$  (27.7%), respectively, as most hydrophobic solvents do. A shallow minimum is also observed in the NMF plot [5,26] at  $x = \sim 0.12$  (30.9%) with a change of the gradient  $d\phi_V/dx$  at  $x = \sim 0.52$  (78%). Solvents that produce a minimum in  $\phi_V = f(x_{\text{sol}})$  in their water mixtures increase hydrogen bonding between the water molecules as DMF does [27,28] and they behave as structure makers. Solvents such as FA that form hydrogen bonds with water have a gradual increase in  $\phi_V$ . In these solvent/water mixtures the interactions between the water molecules are replaced by weaker interactions between FA–water molecules. NMF has an intermediate position in the amide series as it comes from the slopes  $A_V$  of the  $\phi_V$  vs  $m$  curve and their correlation with the pair interaction term in the McMillan–Mayer approach of solutions [24,29], which is a measure of hydrophobic character of the cosolvent.

In Fig. 4 we have plotted  $V_2^0$  against the mixed solvent composition for all the cosolvent/W mixtures. From a first reading, we observe characteristic minima and maxima of the plot of  $V_2^0$  vs composition, which could be related to extrema observed in the behavior of mixed solvents which are interpreted usually in terms of structural changes in the solvent, including H bonding and/or hydrophobic solvation [12b,30–32] but they do not often occur at the same composition in the presence of solute. However, in our case a high coincidence has been found. In the case of EG/W, a pronounced minimum of  $V_2^0$  vs  $x_{\text{sol}}$  is observed at  $x = \sim 0.1$  (27.7%) as does the EG/W solvent in the absence of solute. This corresponds to a high structured arrangement of the EG and water molecules bonded with H bonds which enforce  $\text{C}_{10}\text{Me}_6$  molecules to keep a minimum volume. The  $V_2^0$  of  $\text{C}_{10}\text{Me}_6$  in low compositions of FA/W mixtures is smaller than in water but it becomes higher at  $x = \sim 0.32$  (54%), the

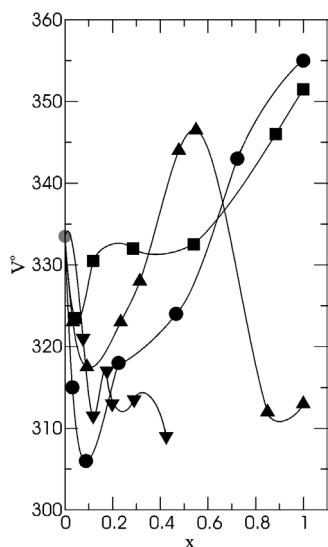


Fig. 4. Apparent molar volumes of  $C_{10}Me_6$  at infinite dilution vs cosolvent composition at 298.15 K in EG/W (●), FA/W (■), NMF/W (▲), DMF/W (▼).

composition where the  $\phi_V$  in the solvent/W mixture tends to steady values. In NMF/W mixtures,  $V_2^0$  takes lower values than in water except in the region 75–80%, where  $V_2^0$  has a maximum that corresponds to the change of the slope at  $x = 0.52$  (78%), of the NMF/W mixture. In DMF/W solvent mixtures,  $V_2^0$  of  $C_{10}Me_6$  decreases continuously with cosolvent composition, and at  $x = \sim 0.12$  (35.15%) a pronounced minimum is observed while, after  $x > 0.3$  (62%), it continues to fall, with a steeper slope.

The differentiation of amide effect in the volumetric behavior of the bolaform is distinct. In the dipolar aprotic DMF, the positive pole is sterically hindered by the two  $-CH_3$  groups from interacting with the negative ions of the solution, while the negative pole on the oxygen atom could be approached by the cations. In the water-rich region of the DMF/W mixture, alkali halides have high  $V_2^0$  values owing to preferential solvation by water molecules of both halide and alkali ions [32,33]. As the composition of DMF is increased, the water molecules are substituted by the DMF molecules, and so the  $V_2^0$  of alkali halides decreases due to the loss of solvation water molecules around cations and the increasing negative electrostrictive effect of the cations on the solvent while the halides ions are prevented from interacting with DMF [32]. In the  $V_2^0$  vs  $x_{sol}$  plot of  $C_{10}Me_6$  in DMF/W (Fig. 4), the  $V_2^0$  values are mostly higher in the water-rich region. At  $x = \sim 0.12$ , a minimum in the  $V_2^0$  vs  $x_{sol}$  is observed which coincides with that of DMF in the mixed solvent. At the same approximate composition, a minimum value in the  $V_2^0$  vs  $x_{sol}$  curve is found in cationic hydrophobic solutes  $Bu_4NBr$  [34] and  $Ph_4PCl$  [32], but not in  $NaBPh_4$  [32], attributed to counterion–solvent interactions, suggesting a similarity in the effect of this solvent mixture on the volume contraction of these large hydrophobic solutes. This similarity is greater between  $C_{10}Me_6$  and  $Bu_4NBr$  as

Table 3

Apparent molar volume at infinite dilution  $\phi_V^0$  ( $cm^3 mol^{-1}$ ) of  $R_4NBr$  and  $C_{10}Me_6$  in pure solvents and water at 298.15 K

	$Me_4NBr^a$	$Et_4NBr^a$	$Pr_4NBr^a$	$Bu_4NBr^a$	$C_{10}Me_6^b$
W	114.3	173.8	239.1	300.4	333.5
EG	110	168.7	237.2	306.3	355
FA	114.9	173.6	242.4	310.5	357.5
NMF		170.5	241.4	310.5	313
DMF		150.5	220	290.4	<200

<sup>a</sup> Ref. [16] and references therein.

<sup>b</sup> This work.

the minimum occurs at  $x = \sim 0.12$ , with a decrease in  $V_2^0$  of  $Bu_4NBr$   $\sim 3\%$  while in  $C_{10}Me_6$  6.5%, suggesting a greater effect of the twofold number of bromide counterions in the solution. The minimum in  $Ph_4PCl$  is observed in a little higher composition  $\sim 0.17$ , indicating a slight effect of the nature of the counterion. Finally, as the sterically hindered positive end of the DMF prevents the interactions with bromide anions the behavior of  $V_2^0$  is controlled mainly by the cations. The divalent but large cations of  $C_{10}Me_6$  exert a negligible electrostriction on the solvent and consequently the structural effects (discussed below in more detail with the transfer volume of ions) of hydrophobic cations account for the semantic decrease of  $V_2^0$ . Also, the weakly hydrophobic molecules of DMF could penetrate between the folding alkyl chains contributing to the decrease of  $V_2^0$ . The same seems to happen at high NMF compositions in NMF/W solvent mixtures and in pure NMF. Here the positive pole of the NMF dipole is partially hindered by one  $-CH_3$  group and an abrupt decreasing of  $V_2^0$  starts at higher NMF composition ( $x = \sim 0.6$ ) than in DMF/W solutions ( $x = \sim 0.4$ ). A minimum in  $V_2^0$  is observed at  $x \sim 0.09$  where a minimum in mixed solvent also exists and is attributed to counterion interactions. The decrease of  $V_2^0$  in high NMF compositions is less than in DMF and it is consistent with the previous for DMF reasoning. The plot of  $V_2^0$  as a function of solvent composition in FA/W and EG/W mixtures is characteristic of hydrogen-bonded solvents where the minima observed correspond to a more structured solvent. In the EG- or FA-rich region,  $V_2^0$  increases with composition and in the pure protic solvent  $V_2^0$  is much larger than in water as hydrophobic hydration in the water-rich region is accompanied with a contraction of volume.

As  $C_{10}Me_6$  is a bi-bromide symmetrical molecule with two tetramethylammonium ions at both ends of the hydrocarbon chain, it seems interesting to compare the  $V_2^0$  with that of the spherically symmetrical tetraalkylammonium bromides ( $R_4NBr$ ) in the same solvents (Table 3).

According to the values of Table 3, the  $V_2^0$  of  $C_{10}Me_6$  and of all the electrolytes in FA are greater than  $V_2^0$  in water while in DMF they are lower. The difference is increased as the molecule of the  $R_4NBr$  becomes larger as also observed in  $C_{10}Me_6$ . The  $V_2^0$  of  $C_{10}Me_6$  in DMF is impressively low. A reasonable assumption is that  $C_{10}Me_6$  possesses twofold the number of bromide ions than  $R_4NBr$ .  $V_2^0$  of  $R_4NBr$  and

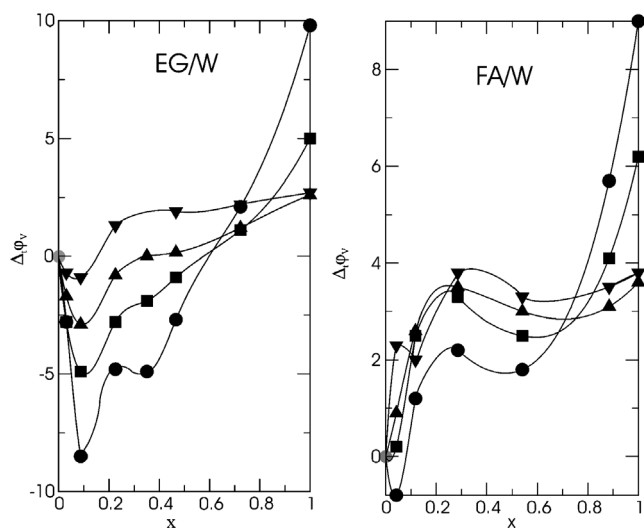


Fig. 5. Transfer volume of  $C_{10}Me_6$  from water to EG/W and FA/W mixtures vs cosolvent composition at the following fixed concentrations: 0.04 (●), 0.102 (■), 0.25 (▲), 0.72 (▼).

$C_{10}Me_6$  in EG are higher than in water in comparison with smaller  $R_4NBr$ , declaring that the size of solute molecules influences the volumetric effect of EG.

Usually in a ternary system, a better insight into the effect of mixed solvent composition on the volumetric properties of the solute offers an examination of the transfer apparent molar volume  $\Delta_t\phi_V$  at a fixed concentration of the solute over a wide range of compositions of the cosolvent relative to water. The transfer volume of solute from water (W) to the solvent mixture (W/S) is defined as

$$\Delta_t\phi_V(W \rightarrow W/S) = \phi_V(W/S) - \phi_V(W), \quad (4)$$

where  $\phi_V(W/S)$  and  $\phi_V(W)$  are the apparent molar volume of the solute at a fixed concentration in the water/solvent mixture and in water, respectively. It is obvious that  $\Delta_t\phi_V(W \rightarrow W/S)$  reflects more clearly the effect of solvent properties as the intrinsic volume of the ions, included in both  $\phi_V(W/S)$  and  $\phi_V(W)$ , is removed and it offers a measure of the difference in ion–solvent interactions between water and S/W mixtures. According to Eqs. (3) and (4), the transfer standard molar volume  $\Delta_tV_2^0(W \rightarrow W/S)$  equals  $\Delta_t\phi_V(W \rightarrow W/S)$  at low fixed concentrations of the solute, as the ion–ion interactions are negligible in this case [30,35].

The transfer volumes, obtained at concentrations 0.04, 0.102, 0.25, 0.72  $m$  of  $C_{10}Me_6$  for all solvent mixtures, are shown in Figs. 5 and 6. The values of 0.04 and 0.102  $m$  were chosen to be in the low concentration range in order to minimize ion–ion interactions. On the other hand, experimental errors existing in lower than 0.04  $m$  concentrations are avoided [11,15–18]. In addition, these concentrations are low enough for any kind of aggregation or cation–cation association that may occur [8,11]. The concentration 0.25  $m$  is an intermediate concentration where large DHLL deviations exist, while 0.72 is a high concentration in the region where  $\phi_V$  values are approximately constant in our case and

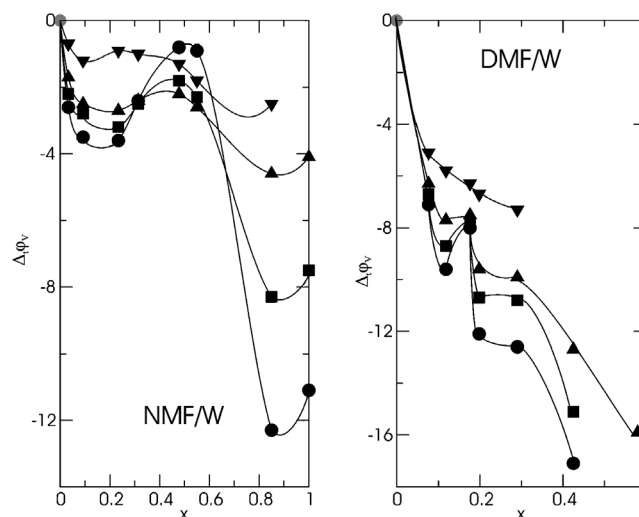


Fig. 6. Transfer volume of  $C_{10}Me_6$  from water to NMF/W and DMF/W mixtures vs cosolvent composition at the following fixed concentrations: 0.04 (●), 0.102 (■), 0.25 (▲), 0.72 (▼).

the effects of ion–ion and ion–solvent interactions are very pronounced.

The transfer volumes  $\Delta_t\phi_V(W \rightarrow W/S)$  or simply  $\Delta_t\phi_V$  of  $C_{10}Me_6$  for a given solvent as a function of  $x_{sol}$  have a similar behavior as  $V_2^0$  vs  $x_{sol}$ , but are more reliable because of the minimization of the errors comparatively with the partial molar volume at infinite dilution. In the water-rich region, the plots of  $\Delta_t\phi_V$  vs  $x_{sol}$  show a similar behavior for all fixed concentrations, except the plot for FA which presents a minimum only at the fixed concentration 0.04  $m$  in the composition  $x = 0.042$  of FA/W.

A noteworthy differentiation is observed in the cosolvent-rich region where  $\Delta_t\phi_V$  of EG and FA are increased unlike the changes of NMF and DMF. The  $\Delta_t\phi_V$  at  $x_{sol} > 0.6$  for EG shows a transition from negative to positive values of  $\Delta_t\phi_V$  with a simultaneous inversion of the  $\Delta_t\phi_V$  values of the lower fixed concentrations over those of higher fixed concentrations. This composition could be considered as the threshold of the solvent-rich region where significant ion–cosolvent interactions occur. So, the lower  $\Delta_t\phi_V$  values of low  $C_{10}Me_6$  concentrations (0.04, 0.102) turn to higher values in high  $C_{10}Me_6$  concentrations (0.72). The same inversion is observed for  $\Delta_t\phi_V$  in FA/W solutions. This inversion happens between positive  $\Delta_t\phi_V$  values, while in NMF and DMF,  $\Delta_t\phi_V$  continuously decrease. In the water-rich region of all solvent mixtures and for all fixed concentrations, the shape of the  $\Delta_t\phi_V$  curves is more or less the same with a diminished depth of the minimum, suggesting that the particular character of the W/S mixture is determinant even the high concentrations of  $C_{10}Me_6$ .

The partial molar volume at infinite dilution of an ion in aqueous solution is made up from the following contributions,

$$V^0(\text{ion}) = V_{\text{int}} + V_e + V_{\text{str}}, \quad (5)$$

where  $V_{\text{int}}$  is the intrinsic volume of the ion and it is equal to its crystallographic volume.  $V_e$  is the electrostriction volume due to the compression of solvent molecules by the ion and it is a negative term in this equation.  $V_{\text{str}}$  is the volume concerning the structural changes around the ions and consists of a negative term responsible for the accommodation of an ion in cavities of the solvent “array” and a positive term responsible for the reinforcement of the solvent structure around the solute ions [15,16]. The same contributions influence the  $V_2^0$  of an electrolyte, although some effects produced by cations may be canceled by the anions. In  $\Delta_t\phi_V$ , the electrostriction term, although negligible for large hydrophobic ions, is removed according to Eq. (4) and so,  $\Delta_t\phi_V$  reflects the effect of solvent properties and structure. In the solvent-rich region, the solvent medium becomes less hydrophobic and the hydrocarbon chain is more relaxed in this environment. In our case, the trend of  $\Delta_t\phi_V$  change depends on the balance of the two structural effects in relation to the accommodation of both bolaform cations and bromide anions in the solvent. The negative values of  $\Delta_t\phi_V$  in NMF/W, DMF/W, and in the water-rich region of EG/W denote that the negative volume arising from the accommodation of both cations and anions of  $C_{10}Me_6$  in the interstices of the solvent is ruling this behavior in contrast with FA/W. At this point we may also observe similarity to the behavior of  $C_{10}Me_6$  with  $Bu_4NBr$  as the plots  $\Delta_t\phi_V$  vs  $x$  for EG and FA change according to that of  $Bu_4NBr$  in the *t*-butyl alcohol (TBA/W) mixture [26,27], which is a well-known hydrophobic cosolvent reinforcing the structure of water while that for DMF changes as that of  $Bu_4NBr$  in DMF [34], revealing a parallelism not only of the solvent structure but also of the size of the solute accommodated in the solvent interstices.

As  $\Delta_t\phi_V$  reflects mainly the effect of solvent properties, we would expect a correlation between  $\Delta_t\phi_V$  and dielectric constants ( $\epsilon$ ) of aqueous solvent mixtures. The change of the excess dielectric constant ( $\epsilon^E$ ) as a function of the amide concentration shows positive deviations from the behavior of the ideal mixtures in FA/W with a maximum at 46 mol% FA while in NMF/W and DMF/W shows negative deviations, which are lower in NMF than DMF, with a minimum value at 60 mol% for NMF and 46 mol% for DMF [36].

A coincidence between the maxima and the minima observed on  $\epsilon^E$  vs mol% of the amide–water mixtures and the extrema present in  $V_2^0$  vs  $x_{\text{sol}}$  of our plots is observed. The positive change of  $\epsilon^E$  vs mol% of FA/W is in agreement with the positive change of  $\Delta_t\phi_V$  vs  $x_{\text{FA}}$  and the negative changes of  $\epsilon^E$  vs mol% of NMF and DMF are in agreement with the respective plots in  $\Delta_t\phi_V$  vs  $x_{\text{sol}}$  of our data. These deviations are qualitatively due to loose (in unsubstituted amides) or dense (in monosubstituted and disubstituted amides) structures of the aqueous solvent mixtures [36]. These different structures reflected by the different sign of  $\epsilon^E$  are a reason for the behavior of  $\Delta_t\phi_V$ . From this view, a correlation of the dielectric constant with  $\Delta_t\phi_V$  is established.

#### 4. Summary

The manner of the influence on the increasing cosolvent composition depends on the cosolvent molecular structure. The solute–cosolvent interactions show a different effect in the water-rich region than in the cosolvent-rich region in all cases studied. Characteristic minima and maxima in the plots of standard molar volume of the bolaamphiphile as a function of the cosolvent composition are related to extrema in the behavior of mixed solvents that reflect the structure of solvent mixture. The minima in the  $V_2^0$  plots attributed to counterion–solvent interactions are in our case of the divalent bolaamphiphile deeper than in other large monovalent solutes, suggesting a greater effect of the twofold number of bromide counterions in the solution and support the generative reasoning of these minima.

The transfer volumes in different cosolvents reflect mainly the effect of solvent structure. In the case of amides, the consecutive substitution of hydrogen in the amide group by methylene reveals the effect of steric factors, arising from the cosolvent, on the volumetric properties. The pronounced decrease of  $\Delta_t\phi_V$  in DMF/W mixture, diminished in NMF/W, could be attributed to a lipophobic penetration of the  $CH_3$  groups between the hydrocarbon chains of  $C_{10}Me_6$  and the significant negative contribution of electrostriction around  $Br^-$  while in FA the reinforcement of the solvent structure overcomes the negative terms of the electrostriction (small enough as FA has high dielectric constant).

The change of  $\Delta_t\phi_V$  as a function of solvent composition in different fixed concentrations although has the same pattern of behavior in low cosolvent compositions, in the rich cosolvent region shows an inversion of the plots of the lower fixed concentrations over those of higher which is related to changes in the solvent structure induced by  $C_{10}Me_6$ . These structures depend on the possibility for the accommodation of solute ions in cavities of the solvent structure, the strength of solvent molecules interactions and the electrostriction caused by the  $Br^-$  ions. The consideration of low and high fixed concentrations detects the change of solute–solvent interactions and/or solvent structure, induced by the high solute concentration.

Finally, a remarkable correlation of the change of  $\Delta_t\phi_V$  vs  $x_{\text{sol}}$  with the excess dielectric constant of the solvent mixture brings up this last function, the concrete factor of the solute volumetric behavior.

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