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Activity coefficients of NaCl in aqueous mixtures with ε-increasing co-solvent: N-methylformamide–water mixtures at 298.15 K

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Dedicated to Professor Dr. Cesar Rodríguez, Dr. Bernardo Domínguez, Dr. María Luisa Llorente, and Dr. Mercedes Lemus on the occasion of their retirement after many years at the University of La Laguna.

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ABSTRACT

The electromotive force of the cell containing two ion-selective electrodes (ISE), Na–ISE|NaCl(m), N-methylformamide (Y), H_2O(100-Y) Cl–ISE has been measured at 298.15 K as a function of the weight percentage Y of N-methylformamide in the mixed solvent. Y was varied between 0 and 100% in ten-unit steps and the molality of the electrolyte (m) was between ca. 0.04 and saturation. The values of the apparent standard electromotive force, E^{0^*} (molal scale), were determined using routine methods of extrapolation together with extended Debye–Hückel (DH), Scatchard (S), Pitzer (P), and modified three-characteristic-parameter-correlation (TCPC) models. The results obtained produced good internal consistency, within the normal limits of experimental error encountered in these types of measurement. Once E^{0^*} was determined, the mean ionic activity coefficients for NaCl, the standard Gibbs energy of transfer from the water to the N-methylformamide–water mixture, the standard solubility product and the primary NaCl hydration number were calculated. The variation of these magnitudes with the composition of this aqueous mixture with ε-increasing co-solvent is discussed in comparison with those containing formamide (ε-increasing co-solvent) and N,N-dimethylformamide (ε-decreasing co-solvent) in terms of the ion-solvent and ion-ion interactions and their changes with the properties of the medium.

1. Introduction

Aquo-organic electrolyte solutions are important for a wide number of applications, and therefore new data are constantly required. In previous works by our group, the behaviour of some alkali halides has been studied both in organic–water mixtures with ε-decreasing co-solvent (i.e. methanol–water, ethanol–water, PEG–water) [1–8], as in organic–water mixtures with ε-increasing co-solvent (i.e. ethylene carbonate–water, formamide–water) [9–13]. A simple methodology was developed and applied to obtain the maximum possible information about these systems. Thus, for example, the activity coefficients were correlated as a function of the properties of the solvent, as expressed by its dielectric constant. The standard Gibbs energy of transfer from the water to the organic–water mixture, the standard solubility product and the primary hydration number of the electrolyte were also calculated and their variation with the composition of the mixture comparatively discussed.

In the literature there are numerous potentiometric studies of NaCl in aqueous mixtures with ε-decreasing co-solvent [1,5,14–30] but very few in aqueous mixtures with ε-increasing co-solvent [11,12,30]. The objective of the present research is to carry out a study for NaCl in N-methylformamide–water mixtures and to compare the results with those obtained previously for NaCl in formamide–water mixtures (ε-increasing co-solvent) [11]. The values reported in the literature for the N,N-dimethylformamide–water mixtures (ε-decreasing co-solvent) [28,29] will be also included in this comparison.

Aqueous mixtures containing amides (in particular, cyclic amides) constitute an important tool in the interpretation of behaviour of complex molecules with biological interest [31,32]. A lot of work has been published on amide–water system to learn the manner in which water exercises thermodynamic and kinetic control over the chemical activities of polypeptides. The abnormally high density of H-bonds in water (strongly self-associated) and the nature donor–acceptor (–CO–NH–peptide bond) gives these water-amide systems a great interest from a structural perspective. The additional presence of an electrolyte further complicates the picture (structure making or breaking effects).

Table 1 summarizes some of the most important properties of the amides studied together with those of water [33–35]. Also, in Fig. 1 the dependency, on the medium composition, of the dielectric constant, density, and viscosity of these amide–water mixtures is shown.

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Table 1
Some physical constants for water (W), formamide (F), N-methylformamide (NMF) and N,N-dimethylformamide (DMF) at 298.15 K.

		Water (W)	Formamide (F)	N-methylformamide (NMF)	N,N-dimethylformamide (DMF)
Molecular weight	M_w	18.015	45.041	59.068	73.094
Molar volume	V (cm^3 mol^{-1})	18.1	39.9	59.1	77.4
Boiling point	bp (K)	373.15	483.65	453.15	426.15
Melting point	fp (K)	273.15	275.70	269.35	212.75
Density	ρ (g cm^{-3})	0.9971	1.1297	0.9988	0.9440
Viscosity	η (mPa s)	0.890	3.302	1.650	0.802
Surface tension	γ (N/m)	0.0718	0.0582	0.0395	0.0364
Dielectric constant	ε_r	78.38	109.57	182.40	36.71
Refractive index	n_D	1.3325	1.4468	1.4300	1.4282
Dipole moment	μ (D)	1.82	3.37	3.86	3.86
Solubility parameter	δ (J$^{1/2}$ cm$^{-3/2}$)	48.1	39.3	20.3	24.8
Polarizability	α (10^{-30} m^3)	1.46	4.23	6.05	7.90
Donor number	DN (kcal mol^{-1})	18.0	24.0	27.0	26.6
Acceptor number	AN (kcal mol^{-1})	54.8	39.8	32.1	16.0

By increasing the amount of co-solvent, the properties of the organic–water mixtures change. Thus, in contrast to N,N-dimethylformamide–water mixtures, both N-methylformamide–water and formamide–water mixtures exhibit an increase in dielectric constant. In the formamide–water mixture the dielectric constant shows a maximum at about 80–90% while the N-methylformamide–water shows a monotonous increase of ε_r which overcome the corresponding values of the formamide–water mixture from 70 wt.%. On the other hand, a small decrease in density is observed both in N-methylformamide–water and N,N-dimethylformamide–water mixtures and a great increase (nearly linear) in the mixture containing formamide. Finally, viscosity shows a continuous increase for formamide–water in contrast to what occurs in the other two mixtures; viscosity maxima occur near 60 wt.% for N,N-dimethylformamide–water and 70 wt.% for N-methylformamide–water.

From the latter two properties (density and viscosity), García et al. [31], calculated excess volumes, mixing viscosities and excess Gibbs energies of activation of viscous flow of the some amide–water mixtures. The values of these functions compared with those of the amide–alcohol mixtures, reveal an important hydration effect with strong amide–water interactions and formation of aggregates, the nature of which depends on the extent of substitution of the amides. Only the behaviour of the formamide–water mixture can be successfully predicted by a simple model.

Also, Papamatthaiakis et al. [32] measured both density and ultrasonic velocity for pure amides and their binary aqueous mixtures. From these data isentropic compressibility, apparent molar compressibility, intermolecular free length and relative association, as well as the corresponding excess quantities were calculated. The systematic study of these parameters reveals a large deviation from ideal behaviour as a result of the strong amide–water interaction.

It is well known [33–35] that, like formamide, N-methylformamide is a highly ionized polar liquid with a dipole moment higher than water and a very large dielectric constant (it has the highest dielectric constant at room temperature of any known liquid). It is a liquid colourless, nearly odourless and completely miscible with water throughout the complete composition range, which forms a hydrogen-bonded network. N-methylformamide is closely related to other amides, notably formamide and N,N-dimethylformamide. However, industrial use is somewhat minor than the latter two. It is mainly used as a reagent in various organic syntheses and in the production of some pharmaceutical compounds. Certain antitumor activities of N-methylformamide have been estimated.

With regard to the used electrolyte, it is well known that NaCl is present in many natural systems, from seawater to biological fluids such as urine. It is very soluble in water (6.146 mol kg^{-1} at 298.15 K) and has a smaller capacity for the association and formation of ion pairs.

The studies presented here were carried out using potentiometric techniques which have been greatly improved in recent decades mainly due to the development and improvement of the ion-selective electrodes (ISE). These electrodes are not only valuable for analytical use, but also may be employed in determining thermodynamic and transport properties. The electrodes used in the present study are those which have recently been developed, in which a glass membrane is used for the Na$^+$ and a

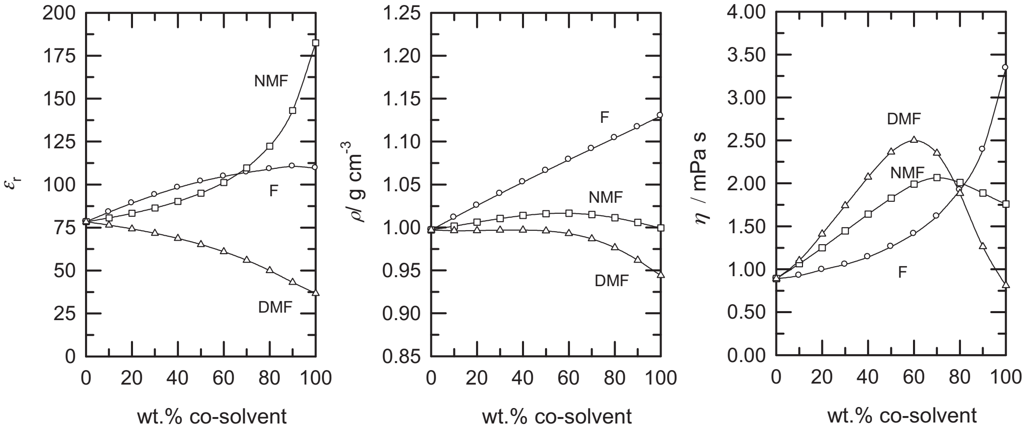

Fig. 1. Composition dependences of relative permittivity (ε_r), density (ρ) and viscosity (η) in formamide (F)–water (○), N-methylformamide (NMF)–water (□) and N,N-dimethylformamide (DMF)–water (△) mixtures at 298.15 K.