

Activity coefficients of NaF in aqueous mixtures with ε -increasing co-solvent: *N*-methylformamide-water mixtures at 298.15 K[☆]



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ABSTRACT

The potential of the cell Na-ISE | NaF (*m*), *N*-methylformamide (*Y*), H₂O (100-*Y*) | F-ISE, which contains two selective electrodes (*bi*-ISE cell), has been measured at 298.15 K as a function of the weight percentage, *Y*, of *N*-methylformamide in a mixed solvent and the molality of NaF. *Y* was varied between 0 and 80% in ten-unit steps, and the molality of the electrolyte (*m*) was between approximately 10^{−4} mol kg^{−1} and the saturation point. The values of the average apparent standard potential, E^{0*} (molal scale), were determined using habitual methods of extrapolation together with the extended Debye-Hückel (DH), Scatchard (S), and Pitzer (P) equations. The obtained results provided good internal consistency within the normal limits of experimental error encountered in these types of measurements. Once E^{0*} was determined, the mean ionic activity coefficients for NaF were calculated and subsequently modeled according to the TCPC (modified three-characteristic-parameter-correlation) method. Additionally, the values of the total standard Gibbs energy of transfer from the water to the *N*-methylformamide (NMF) – water mixture, their ionic contributions, the standard solubility product, and the NaF primary hydration number were also determined. The variations of these magnitudes with the composition of the aqueous mixture are discussed in terms of ion-solvent and ion-ion interactions as a function of the properties of the medium.

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1. Introduction

Activity coefficients and related thermodynamic quantities (e.g., osmotic coefficients, water activities, changes in the standard Gibbs energy of transfer, standard solubility products, etc.) remain in constant demand by researchers in chemistry related disciplines, including potentiometry, polarography, voltammetry, biochemistry, geochemistry, industrial chemistry, pharmaceuticals, medicinal chemistry, veterinary and food chemistry, environmental and oceanographic chemistry, water decontamination, purification and desalination treatments, petroleum recovery processes, and electroanalytical methods.

Knowledge of activity coefficients is crucial to determine

deviations from the ideal behavior of real solutions, such as those containing electrolytes [1–3]. As is known, activity coefficients can be determined using different methods [4], the most common of which are isopiestic and potentiometric techniques. The former approach, which based on the balance of vapor pressures between a working solution and a reference solution, allows us to determine the osmotic coefficients, from which the activity coefficients are then derived. It is a laborious, tedious and slow method, and it is not very accurate when working with mixed solvents because of the different vapor pressures of the mixture components. In contrast, the potentiometric method is faster, less tedious and gives the activity coefficients directly without significant interference from the solvent mixture. However, this latter method has a decisive limitation; that is, the electrodes for the ions that constitute the investigated electrolyte must be reversible. Until the 1960s, cells were mainly used with combinations of electrodes of low impedance, such as gasses; metal electrodes of the first type; electrodes of the second type containing silver – salts of silver or

[☆] Dedicated to our technician D. Miguel Rojas Morales on the occasion of his retirement after many years of service at the Universidad de La Laguna.

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mercury – mercury salts, electrodes of amalgam of mercury; and so on [1–4]. Since the 1960s, cells with one selective electrode ion (ISE) have been used, which have high impedance, and one of those cited previously of low impedance. Additionally, for the past 20 years, cells containing two ISE of high impedance have been used. Experiments using electrodes with high impedance (i.e., resistance greater than 10^{13} or 10^{14} Ω) must be performed with caution. In such cases, the electrical currents that circulate through the system (i.e., the electrodes more than the solution) are lower than 10^{-13} or 10^{-14} amps, and these tiny currents can be easily affected by electromagnetic fields, which can cause fluctuations in the potentials and make them difficult to measure. In fact, these measurements are so sensitive that movement close to the equipment can lead to variations in the potential. To prevent such fluctuations, *bi-* or *tri-*axial small length cables are used so that the cables they do not act as receiving antennas, Faraday cages are used to avoid electrostatic interactions, and ground connections, filters to avoid electronic noise, etc., are also used.

The vast majority of activity coefficients measurements have been performed using water as the solvent [1–6]. However, aqua-organic electrolyte solutions are important for a wide range of applications, for example, *drowning-out* process [7,8], design and simulation of operations, including the construction of phase or solubility diagrams, liquid-liquid extraction, model study and validation, and the correlation and prediction of solubility and vapor-liquid equilibrium, to name a few [7–13].

In previous work by our group, the behaviors of some alkali halides have been examined both in organic-water mixtures with an ϵ -decreasing co-solvent (i.e., methanol-water, ethanol-water, sugar-water, PEG-water) [14–25] and in organic-water mixtures with an ϵ -increasing co-solvent (i.e., ethylene carbonate-water, formamide (FA)-water, *N*-methylformamide (NMF)-water) [26–32]. We define mixtures ϵ -decreasing those in which the co-solvent has a dielectric constant less than water and therefore, increasing its concentration decreases the dielectric constant of the mixture. In contrast, we define mixtures ϵ -increasing which the co-solvent has a dielectric constant greater than water, which increases the dielectric constant of mixture as the concentration of the co-solvent increases. It should be noted that, in either case, the mixtures of solvents is the standard state. Thus, they are binary mixtures consisting of an electrolyte and a mixed solvent. It is true, therefore, that $\gamma(m = 0) = 1$ at infinite dilution regardless of the composition of the mixture.

In this work we have examined binary mixtures consisting of the electrolyte NaF and the mixed solvent NMF-water between 0 and 80% in ten-unit steps. For both the 90% and 100% solutions, the solubility of NaF is very small and the consequent range of molalities to investigate is too short, not allowing to get results consistent. The unusually high density of H-bonds in water (strongly self-associated) and the donor-acceptor character of NMF (i.e., the peptide–NH–CO– bond) make these water-amide systems incredibly interesting from a structural point of view. Moreover, the additional presence of an electrolyte further complicates the system dynamics (i.e., *breaking* or *making* structural effects).

For comparison, Fig. 1 shows the chemical structure of NMF together with that of FA. Table 1 summarizes some of the most important properties relevant of these amides together with those of water [33–35]. Fig. 2 shows the dependency on the medium composition, the dielectric constant, density, and viscosity of these amide-water mixtures [35]. Both the dielectric constant of the medium and its density are required to calculate the constants appearing in the different models that are used to determine the activity coefficients. The dielectric constant provides a measure of the electrostatic behavior of the mixture and possible interactions that may occur in it. In addition, the viscosity indicates if the media

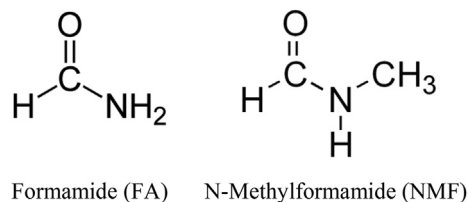


Fig. 1. Chemical structure both Formamide (FA) and *N*-methylformamide (NMF).

is more or less structured [36,37].

Like FA, NMF [33–35] is a highly ionized polar liquid with a dipole moment higher than water and a very large dielectric constant. Indeed, it has the highest dielectric constant at room temperature of any known liquid. NMF is a colorless liquid, nearly odorless and completely miscible with water throughout the complete composition range, forming a hydrogen-bonded network. It is mainly used as a reagent in various organic syntheses and in the production of some pharmaceutical compounds. Moreover, specific antitumor activities of *N*-methylformamide have been reported. According to Marcus [35], water self-interaction is not favored in aqueous-NMF mixtures. The superior compatibility of this co-solvent with water over FA with water is surprising.

NaF presents a solubility limit ($0.983 \text{ mol kg}^{-1}$ in water to 298.15 K) that is much lower than that for other sodium halides such as NaCl (6.15 mol kg^{-1}), NaBr (9.19 mol kg^{-1}), and NaI ($12.27 \text{ mol kg}^{-1}$), and other alkaline fluorides such as KF ($17.50 \text{ mol kg}^{-1}$), RbF ($28.72 \text{ mol kg}^{-1}$), and CsF ($24.16 \text{ mol kg}^{-1}$). Only LiF ($0.052 \text{ mol kg}^{-1}$) exhibits a solubility less than NaF. As shown by Robinson et al. in their studies of activity and conductivity in water [38,39], NaF can help to form ion-pairs in both activity and conductivity studies in water. The ability to form ion-pairs is enhanced in media of low dielectric constant [17], whereas it virtually disappears in media of high dielectric constant [27].

The results presented herein were generated using potentiometric techniques that have been greatly improved in recent decades, primarily because of the development of ion-selective electrodes (ISEs) and their improvements. The measurements were performed at 298.15 K because very few data of both the dielectric constant and density of these mixed solvents are available at other temperatures.

2. Experimental

NaF, Merck pro analysi ($w \geq 0.99$), was vacuum-dried at 373 K for 72 h and then stored in a desiccators over silica-gel, P_2O_5 , and CaO anhydrous. NMF, Sigma-Aldrich puris ($w = 0.99$), was used without prior treatment (see Table 2). Corrections to account for the very small water content within the original product were considered unnecessary. For the experiments, Millipore double deionizer water was *bi*-distilled by adding $KMnO_4$ and NaOH in a first flask to remove the organic matter; subsequently, drops of H_3PO_4 were added to a second flask to neutralize the pH until $\kappa < 10^{-6} \text{ S cm}^{-1}$ and pH 6.8–7.2 were obtained.

All solvents were prepared by directly weighing the water and amide on a Mettler PM2000 balance with resolution of 0.01 g. For each set of experiments (corresponding to a wt.% of NMF), working solutions were obtained by successively adding weighed amounts of solid NaF in a Mettler AE163 balance with a resolution of 0.1 mg. The molality uncertainty can be estimated to be approximately $\pm 0.0001 \text{ mol kg}^{-1}$. The solutions were continuously stirred using a magnetic stirrer to avoid concentration or temperature gradients. Such agitation also elicits a “mysterious” effect that causes the

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