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Thermodynamics of amide + amine mixtures. 4. Relative permittivities of *N*,*N*-dimethylacetamide + *N*-propylpropan-1-amine, + *N*-butylbutan-1-amine, + butan-1-amine, or + hexan-1-amine systems and of *N*,*N*-dimethylformamide + aniline mixture at several temperatures. Characterization of amine + amide systems using ERAS

Fernando Hevia, Juan Antonio González *, Ana Cobos, Isaías García de la Fuente, Luis Felipe Sanz

G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, Paseo de Belén, 7, 47011 Valladolid, Spain

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ABSTRACT

Relative permittivities at 1 MHz, ε_r, and at (293.15–303.15) K are reported for the binary systems *N*,*N*-dimethylacetamide (DMA) + *N*-propylpropan-1-amine (DPA), + *N*-butylbutan-1-amine (DBA), + butan-1-amine (BA) or + hexan-1-amine (HxA) and for *N*,*N*-dimethylformamide (DMF) + aniline. The excess permittivities, ε_r^E, are large and negative for systems with DMA, whereas they are large and positive for the aniline mixture. From the analysis of these ε_r^E data and of measurements previously reported, it is concluded: (i) the main contribution to ε_r^E in systems with linear amines arises from the breaking of interactions between like molecules; (ii) in the DMF + aniline mixture, interactions between unlike molecules contribute positively to ε_r^E, and such a contribution is dominant; (iii) longer linear amines are better breakers of the amide-amide interactions; (iv) interactions between unlike molecules are more easily formed when shorter linear amines, or DMF, participate. These findings are confirmed by a general study conducted in terms of excess values of molar orientational and induced polarizabilities and of the relative Kirkwood correlation factors for systems and components. The ERAS model is also applied to amide + amine mixtures. ERAS represents rather accurately the excess enthalpies and volumes of the mentioned systems. The variation of the cross-association equilibrium constants, determined using ERAS, with the molecular structure is in agreement with that observed for ε_r^E.

1. Introduction

The chemical environment of proteins is highly complex. A suitable approach for its investigation is to focus on small organic molecules which are more or less similar to the functional groups which constitute the biomolecule [1]. In this framework, the determination of thermodynamic, transport and dielectric properties for the mentioned molecules and for their mixtures is necessary, as information on interactions in condensed phase environments can be inferred from these properties.

Amides are a very important class of organic solvents due to their high polarity (the dipole moment of *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMA) is 3.7 D [2,3]), strong solvating power and liquid state range [4]. The latter is strongly linked to the ability of amides to form hydrogen bonds. It is well known that primary and secondary amides are self-associated species, while tertiary amides show a relevant local order due to the existence of strong dipolar interactions between their molecules [5,6]. This makes amides useful as model systems for peptides [6].

The amine group is also encountered in substances of great biological interest. For example, histamine and dopamine act as neurotransmitters [7,8], and the breaking of amino acids releases amines. On the other hand the proteins usually bound to DNA polymers contain various amine groups [9]. Interestingly, primary and secondary amines are self-associated compounds [10–14] with low dipole moments in the case of linear amines (1.3 D for BA and 1.0 D for DPA [15]). The dipole moment of aniline (1.51 D [3]) is higher and proximity effects between the phenyl ring and the amine group lead to strong dipolar interactions between aniline molecules. As a consequence, aniline + *n*-alkane mixtures are characterized by relatively high upper critical solution temperatures (343.1 K for the heptane solution [16]).

* Corresponding author.
E-mail address: jagl@termo.uva.es (J.A. González).

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The study of amine + amide systems is then relevant as it allows to gain insight into the amide group behaviour when it is surrounded by different environments. In fact, the hydrogen-bonded structures where the amide group is involved can show very different biological activities depending on the mentioned environments [17].

The few data available in the literature on excess molar enthalpies, H_m^E, for amine + amide mixtures underline the importance of interactions between unlike molecules in such systems. For example, at equimolar composition, we have $H_m^E/J \cdot mol^{-1} = -2946$ (aniline + DMF, $T = 298.15$ K) [18]; −352 (aniline + DMA, $T = 298.15$ K) [19], −1000 (HxA + *N*-methylacetamide (NMA), $T = 363.15$ K) [20]. Interestingly, H_m^E /J·mol^{-1} values of methanol + NMA (−76, $T = 313.15$ K) [21], or + DMA (−737; $T = 298.15$ K) [22] are very different.

In previous studies, we have reported data on density, ρ, speed of sound, c, and refractive index, n_D, for the binary systems DMF [23], or DMA [24] + *N*-propylpropan-1-amine (DPA) or + butan-1-amine (BA) at (293.15–303.15) K, and + *N*-butylbutan-1-amine (DBA) or + hexan-1-amine (HxA) at 298.15 K. These data have been interpreted in terms of solute-solvent interactions and structural effects [23,24]. On the other hand, we have also reported permittivity measurements for the DMF + BA, + HxA, + DPA, + DBA systems at (293.15–303.15) K [25]. As a continuation of these works, we provide now low-frequency relative permittivities, ε_r, for the DMA + BA, + HxA, + DPA, + DBA mixtures, and for the DMF + aniline system at the same temperature range. The replacement of DMF by DMA in the mentioned systems including linear amines may be useful to investigate steric/size effects on the excess ε_r values. The aniline + DMF system has been selected on the basis of its very large and negative H_m^E value. The present study is completed by the application of different theories. Firstly, amine + amide mixtures are studied using the ERAS model [26]. Secondly, the ε_r data reported here are used together with the corresponding ρ and n_D values available in the literature [23,24,27] to determine orientational and induced polarizabilities according to the Kirkwood-Fröhlich model [28–31] and the Balankina relative excess Kirkwood correlation factors [32], very useful quantities to gain insight into the dipole correlations present in the mixtures under consideration.

2. Experimental

2.1. Materials

Table 1 collects information regarding the source and purity of the pure compounds, which have been used with no further purification.

2.2. Apparatus and procedure

Binary mixtures were prepared by mass in small vessels of about 10 cm^3, using an analytical balance Sartorius MSU125p (weighing accuracy 0.01 mg), with all weighings corrected for buoyancy effects. The standard uncertainty in the final mole fraction is estimated to be 0.0010. Molar quantities were calculated using the relative atomic mass Table of 2015 issued by the Commission on Isotopic Abundances and Atomic Weights (IUPAC) [33]. In order to minimize the effects of the interaction of amines with air components, they were stored with 4 Å molecular sieves; also, the measurement cell (see below) was completely filled with the samples and appropriately closed. Different density measurements of pure compounds, conducted along experiments, showed that this quantity remained unchanged within the experimental uncertainty.

Temperatures were measured by means of Pt-100 resistances, calibrated according to the ITS-90 scale of temperature, against two fixed points: the triple point of water and the fusion point of Ga. The standard uncertainty of the equilibrium temperature measurements is 0.01 K and the corresponding accuracy is 0.02 K.

Permittivity measurements were conducted using a 16452A cell (parallel-plate capacitor) connected, by means of a 16048G test lead, to a precision impedance analyser 4294A; all of them are from Agilent. The 16452A cell is made of Nickel-plated cobalt (54% Fe, 17% Co, 29% Ni) with a ceramic insulator (alumina, Al_2O_3). The volume of the sample filling the cell is ≈ 4.8 cm^3. The temperature was controlled by a thermostatic bath LAUDA RE304, (temperature stability: 0.02 K). Details about the device configuration and calibration can be found elsewhere [34]. The relative standard uncertainty of the ε_r measurements (i.e. the repeatability) is 0.0001. The total relative standard uncertainty of ε_r was estimated to be 0.003 from the differences between our data and values available in the literature for the following pure liquids in the temperature range (288.15–333.15) K: water, benzene, cyclohexane, hexane, nonane, decane, dimethyl carbonate, diethyl carbonate, methanol, 1-propanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol.

Our experimental ε_r values, at 1 MHz and 0.1 MPa, of pure compounds, together with literature data, are shown in Table 2. We note the excellent agreement encountered between them for DMF and DMA. Larger discrepancies between such data are observed for amines, which may be ascribed to the different source and purity of the amines used in the literature. In fact, inspection of Table 2 shows that, for example, some ε_r values of aniline taken from the literature are not sure as they do not change consistently with temperature. In contrast, our ε_r values correctly decrease with the increasing of temperature, and the density measurements are in good agreement with literature data (Table S1, supplementary material; see also [23,24] for the remaining amines).

3. Experimental results

The relative permittivity of an ideal mixture at the same temperature and pressure as the solution under study, ε_r^{id}, is calculated from the expression [35]:

$$\varepsilon_r^{id} = \phi_1 \varepsilon_{r1}^* + \phi_2 \varepsilon_{r2}^* \quad (1)$$

Table 1
Sample description.

Chemical name	CAS Number	Source	Purification method	Purity[a]
N,*N*-dimethylacetamide (DMA)	127-19-5	Sigma-Aldrich	None	0.9998
N,*N*-dimethylformamide (DMF)	68-12-2	Sigma-Aldrich	None	0.9995
N-propylpropan-1-amine (DPA)	142-84-7	Aldrich	None	0.996
N-butylbutan-1-amine (DBA)	111-92-2	Aldrich	None	0.9974
butan-1-amine (BA)	109-73-9	Sigma-Aldrich	None	0.9996
Hexan-1-amine (HxA)	111-26-2	Aldrich	None	0.999
Aniline	62-53-3	Sigma-Aldrich	None	0.999

[a] In mole fraction. Provided by the supplier by gas chromatography.