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Volumetric and refractive index study of the ternary mixture methanol/formamide/acetonitrile at 298.15 K

Filomena Martins [a,*], Ruben Elvas Leitão [a,b], Nélson Nunes [a,b,**]

[a] Centro de Química e Bioquímica (CQB), Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Ed. C8, Campo Grande, 1749-016 Lisboa, Portugal
[b] Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa (ISEL), Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal

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ABSTRACT

The ternary mixture methanol (MeOH)/formamide (Form)/acetonitrile (MeCN) was studied by means of refractive index and density measurements. Data for a total of 22 ternary mole fractions, and 19 binary mole fractions for each formamide containing mixture, as well as values from the previously studied methanol/acetonitrile mixture were obtained and evaluated. Excess properties were computed and modeled by polynomial equations, namely Redlich-Kister for binary fractions and Cibulka for ternary mixtures. Partial molar volumes were likewise calculated and together with previously published values allowed the interpretation of structural effects associated with molecular interactions.

1. Introduction

The study of solvent mixtures is an area of growing interest. Solvent mixtures are widely used in industrial processes and are also important in theoretical studies for model development and solvent parameters' estimation [1].

However, many of these mixtures show non-ideal behavior and both the optimization of processes and the adequate design of equipment depend significantly on the correct assessment of mixing properties.

In previous works, we have carried out a thorough structural characterization of the ternary mixture methanol/propan-1-ol/acetonitrile (MeOH/1-PrOH/MeCN) by means of refractive indices, volumetric properties and solvatochromic probes [2–4].

In this work, we extended the matrix of solvents by replacing in the original ternary mixture the propanol-1-ol component by formamide, a solvent that despite its different chemical nature still assured total miscibility for all ternary and binary fractions. Even though other authors have already partially addressed the binary mixtures methanol-formamide and formamide-acetonitrile [5–10], molar volumes and refractive indices of the ternary mixture have never been measured and still less investigated.

Experimental results were also used to calculate a set of excess and partial molar properties which allowed the interpretation of the mixtures' behavior and the identification of various molecular interactions among the mixtures' components.

As regards the calculation of excess properties, special care was devoted to the accurate definition of excess refractive indices which, to the best of our knowledge, has never been considered in the treatment of these mixtures before. For that purpose, we have used a methodology based on the thermodynamic formalism proposed by Reis et al. [11] which distinguishes between the refractive index of mixing n_D^{E*} and the thermodynamic excess refractive index n_D^E, as putative measures of deviation of n_D from ideality. The refractive index of mixing is given by Eq. (1):

$$n_D^{E^*} = n_D - \sum x_i n_{D_i} = \Delta_{mix,x} n_D \quad (1)$$

where x_i is the mole fraction of each component, n_{D_i} is the refractive index of the pure component, and n_D the refractive index of the mixture. On the other hand, the thermodynamic excess refractive index n_D^E, as proposed by Reis et al., is based on the Maxwell relationship between the refractive index and the relative permittivity and is expressed on a volume fraction basis, ϕ, as suggested earlier by Brocos et al. [12]. Reis et al. define the refractive index of mixing in terms of volume fraction,

* Corresponding author.
** Correspondence to: N. Nunes, Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal.
E-mail addresses: filomena.martins@ciencias.ulisboa.pt (F. Martins), nnunes@deq.isel.ipl.pt (N. Nunes).

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Table 1
Refractive indices, n_D, and densities, ρ, of pure components at 298.15 K, and literature values for comparison purposes.

Component	n_D		ρ/g cm^{-3}	
	Exp.	Lit. [16]	Exp.	Lit. [16]
Methanol	1.3269	1.3265	0.78665	0.7872
Formamide	1.4460	1.446	1.12910	1.1288
Acetonitrile	1.3414	1.341	0.77657	0.7760

$\Delta_{mix,\phi}n_D$, as:

$$\Delta_{mix,\phi}n_D = n_D - n_{D(unmixed)} \quad (2)$$

where $n_{D(unmixed)} = \sum \phi_i n_{D_i}$,and the thermodynamic ideal refractive index of mixture n_D^{id} as:

$$n_D^{id} = \left[\sum \phi_i (n_{D_i})^2\right]^{1/2} \quad (3)$$

From these definitions an expression for n_D^E can thus be developed:

$$n_D^E = n_D - n_D^{id} = n_D - \left[\sum \phi_i (n_{D_i})^2\right]^{1/2} \quad (4)$$

Molar volumes and derived properties such as excess molar volumes are also commonly used to analyze solvent-solvent interactions. Despite this fact the breakdown from raw data to physicochemical information can be quite complex. An increased molar volume can be attributed to different causes: bond breaking of one or all mixture components, non-favorable molecular geometry and/or stereochemical hindrance. Conversely, a decrease of molar volume may result from stronger interactions between mixtures' components, better housing and/or favorable geometry of molecules in the solvent's structural network.

Also, partial molar volumes $\bar{V}_i$ and excess partial molar volumes $\overline{V}_i^E$ can provide further insights into solvent's structure although these properties are scarcely used in the context of these studies and were thus also computed in the present work.

Excess molar volumes, V_m^E, can be calculated using Eq. (5):

$$V_m^E = \sum x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (5)$$

where M_i is the molar mass of component i, ρ_i, the density of the pure component and ρ the density of the mixture, x_i has the same meaning as before.

In addition, partial molar volumes of each component, $\bar{V}_i$, can be calculated from Eq. (6),

$$V_i = V_i^0 + \overline{V}_i^E \quad (6)$$

where V_i^0 is the molar volume of the pure component and $\overline{V}_i^E$ is the excess partial molar volume of component i which is determined, for n component mixtures through Eq. (7) [13]:

$$\overline{V}_i^E = V^E + \left(\frac{\partial V^E}{\partial x_i}\right)_{T,p,x_j \neq x_i} - \sum_{k=1}^{n} x_k \left(\frac{\partial V^E}{\partial x_k}\right)_{T,p,x_j \neq x_k} \quad (7)$$

T stands for temperature, p for pressure and all other symbols have the same meaning as before. This equation for binary mixtures, simplifies to:

$$\overline{V}_i^E = V^E + (1 - x_i)\left(\frac{\partial V^E}{\partial x_i}\right)_{T,p} \quad (8)$$

Furthermore, to highlight the excess properties' variation over the whole mole fraction domain, fitting polynomials can be used, namely in the case of ternary mixtures the Cibulka equation [14], Eq. (9):

$$Y_{123}^E = Y_{12}^E + Y_{13}^E + Y_{23}^E + \beta_1\beta_2\beta_3(A + B(\beta_1 - \beta_2) + C(\beta_2 - \beta_3)) \quad (9)$$

where Y_{123}^E refers to the values of V_m^E, n_D^{E*}or n_D^E, in the ternary mixtures, Y_{12}^E, Y_{13}^E, Y_{23}^E to the corresponding values in the binary mixtures, β_1, β_2, β_3, represent either mole fractions (in the first two cases) or volume fractions (in the latter case) of components 1, 2 and 3 and A, B, C are the polynomial coefficients calculated using a standard least-squares fitting method.

On the other hand, binary excess properties can be readily fitted to a Redlich-Kister type equation [15]. For a mixture with two components, 1 and 2, the expression for Y_{12}^E assumes the form of Eq. (10):

$$Y_{12}^E = \beta_1\ \beta_2 \sum_{i=0}^{n} a_i (\beta_1 - \beta_2)^i \quad (10)$$

where a_i designates the polynomial coefficients calculated using a standard least-squares fitting method, and all other symbols have the same meaning as above.

Table 3
Regression parameters of the Cibulka fit for the refractive index of mixing, n_D^{E*}, excess refractive index, n_D^E, and excess molar volume, V_m^E, at 298.15 K.

	n_D^{E*}	$n_D^{E(a)}$	V_m^E/cm^3 mol^{-1}
$A \pm s$ (A)	0.014 ± 0.004	0.025 ± 0.003	−3.0 ± 0.3
R^2	0.989	0.992	0.994
s	0.0006	0.0003	0.03
F	6710	9925	12,812
n	77	78	81

[a] Cibulka fit computed from volume fractions.

2. Experimental section

All solvents used were HPLC grade and were supplied by Sigma–Aldrich. Their purity (>99%) was confirmed by establishing that values obtained for densities and refractive indices agreed with literature values

Table 2
Regression parameters of the Redlich-Kister fit for the refractive index of mixing, n_D^{E*}, excess refractive index, n_D^E, and excess molar volume, V_m^E, at 298.15 K.

	Property	$a_0 \pm s$ (a_0)	$a_1 \pm s$ (a_1)	$a_2 \pm s$ (a_2)	$a_3 \pm s$ (a_3)	R^2	s	F
MeOH/MeCN	n_D^{E*}	0.0095 ± 0.0001	0.0015 ± 0.0002	–	–	0.992	0.00007	1206
	$n_D^{E(a)}$	0.005726 ± 0.00009	–	–	–	0.995	0.00007	4260
	V_m^E/cm^3 mol^{-1}	−0.547 ± 0.007	−0.25 ± 0.03	−0.25 ± 0.03	−0.30 ± 0.06	0.996	0.004	817
MeOH/Form	n_D^{E*}	0.0253 ± 0.0005	0.007 ± 0.001	−0.006 ± 0.002	–	0.995	0.0003	1313
	$n_D^{E(a)}$	0.0226 ± 0.0005	0.008 ± 0.001	−0.00 ± 0.002	–	0.994	0.0003	1057
	V_m^E/cm^3 mol^{-1}	−2.39 ± 0.06	−0.8 ± 0.1	−0.7 ± 0.3	–	0.993	0.04	897
Form/MeCN	n_D^{E*}	−0.0069 ± 0.0003	–	–	–	0.964	0.0002	534
	$n_D^{E(a)}$	0.0185 ± 0.0003	−0.0035 ± 0.0007	–	–	0.996	0.0002	2234
	V_m^E/cm^3 mol^{-1}	−2.29 ± 0.06	–	–	–	0.987	0.05	1525

[a] Redlich-Kister fit computed from volume fractions.