J Solution Chem (2007) 36:1–11
DOI 10.1007/s10953-006-9093-2

ORIGINAL PAPER

Determination of the Apparent Molar Refraction and Partial Molar Volume at Infinite Dilution of Thiophene-, Pyrrole- and Furan-2-Carboxaldehyde Phenylhydrazone Derivatives in Acetonitrile at 293.15 K

Ysaías J. Alvarado · José Caldera-Luzardo ·
Gladys Ferrer-Amado · Victoria Mancilla-Labarca ·
Elba Michelena

Received: 22 March 2006 / Accepted: 14 June 2006 /

Abstract High-precision densitometry and high-accuracy refractometry measurements of extremely dilute solutions of the thiophene-2- (TCPH), pyrrole-2- (PCPH) and furan-2-carboxaldehyde-phenylhydrazone (FCPH) compounds in acetonitrile have been obtained at 293.15 K. The partial molar volumes, V_2^{∞}, of each compound at infinite dilution were determined. The apparent molar refraction of these solutes at infinite dilution at 293.15 K has been experimentally determined within the Kohner-Geffcken-Grunwald-Haley approximation. The volumetric and refractometric results were interpreted in terms of the Pauling electronegativity and intrinsic molar volume of the heteroatom, and the aromaticity of the heterocyclic rings. The experimental results indicate that solute-solute interactions are negligible within the concentration range studied. Theoretical calculations at the DFT-B3LYP/6−311++G(3d,3p) level of molecular volumes support the interpretation that the volumetric contribution from the solute-solvent interactions to the limiting partial molar volumes of solutes are very small and thus solute molecules are isolated in this medium.

Keywords Phenylhydrazone derivatives · Apparent molar refraction · Intermolecular forces · Limiting partial molar volume · Pauling electronegativity

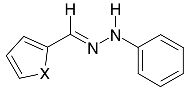
1 Introduction

The phenylhydrazone derivatives have been shown to have remarkable stability, high tendency to form non-centrosymmetry crystal packing and exceptional electronic and chemical properties needed for designing of new electronic devices with technological applications [1]. Although these materials have analytical, inorganic, organic, biological and optical utility [1–3] studies on their fundamental molecular properties are very limited. In fact, the

---

Y. J. Alvarado (✉) · J. Caldera-Luzardo (✉) · G. Ferrer-Amado · V. Mancilla-Labarca · E. Michelena
Laboratorio de Electrónica Molecular (L.E.M), Departamento de Química, Facultad Experimental de Ciencias, La Universidad del Zulia (LUZ), Grano de Oro, Maracaibo, Estado Zulia, República Bolivariana de Venezuela
e-mails: yalvaradofec@yahoo.com; josecldr@yahoo.com

Fig. 1



X= N-H (PCPH); O (FCPH) and S (TCPH)

molecular electronic polarizabilties of these molecular systems both in the gas phase and solution are unknown, possibly due to their poor solubility in common organic solvents and their low volatility [3]. Based on these considerations and continuing with our interest in this field [4], we report in this work the experimental determination of the apparent molar refractions and partial molar volumes of the thiophene, pyrrole and furan-2-carboxaldehyde phenylhydrazone derivatives (henceforth referred as TCPH, PCPH and FCPH, respectively; see Fig. 1) in dilute acetonitrile solutions using high-precision densitometry [4], high accuracy refractometry [4] and a model proposed by Kohner-Geffcken-Grunwald-Haley [5]. It is very important to mention that this refractometric method is particularly useful for compounds with only moderate solubility in a given solvent. The changes induced by the heteroatom of an aromatic five-membered ring moiety on the apparent molar refraction and limiting molar volume at infinite dilution are discussed. Acetonitrile was chosen as the solvent in this study because the phenylhydrazone derivatives are insufficiently soluble in common aprotic solvents and thus this solvent has chromatographic, industrial, biological and chemical importance. In this work we also carry out a comparative study between the partial molecular volumes and apparent molar polarizabilities at infinite dilution and the molecular volumes and electronic molar polarizabilitiy values obtained from fully optimized geometries by using theoretical calculations at the DFT-B3LYP/6−311++G(3,3p) level.

2 Theory

In a two-component system, the apparent molar volume of the solute, $V_{2,\phi}$, can be calculated from the measured densities of the solutions, ρ, through the relationship [6a]:

$$V_{2,\phi} = \left(\frac{M_2}{\rho_1}\right) - 10^3\left(\frac{\rho - \rho_1}{\rho_1 C}\right) \tag{1}$$

where M_2 is the molar mass of the solute, ρ and ρ_1 are the densities of the solution and the solvent, respectively, and C is the molar concentration of the solute. However, for extremely dilute solutions, the $V_{2,\phi}$ values are independent of the concentration. Therefore, by definition, it can be assumed that the $V_{2,\phi}$ values are equal to the partial molar volume of the solute at infinite dilution, V_2^∞, and, as a consequence, V_2^∞ can be estimated by the method of least squares as described in reference [6b]:

$$\rho = \rho_1 + \left(\frac{M_2 - \rho_1 V_2^\infty}{10^3}\right)C \tag{2}$$

Alternatively, V_2^∞ can be calculated as the average value of $V_{2,\phi}$ determined within the studied concentration range [7]. On the other hand, under the same experimental conditions, Kohner [5a], Geffcken [5b], and Grunwald and Haley [5c] have demonstrated that the Lorentz-Lorenz equation for a binary mixture in differential form, retaining only first-order terms of the Taylor series, reduces to

$$\theta = 6000\left(\frac{1}{n_1^2+2}\right)^2 n_1(n-n_1) = \left\{R_{2,\phi} - \left(\frac{n_1^2-1}{n_1^2+2}\right)V_{2,\phi}\right\}C = \Omega_2 C \tag{3}$$

where θ is the relative refraction, $R_{2,\phi}$ is the apparent molar refraction of the solute and n and n_1 are the refractive indexes of the solution and solvent, respectively. However, for highly dilute solutions, Ω_2 is effectively constant [5c] and its value can be determined by the method of least squares. Therefore, $R_{2,\phi}$ and $V_{2,\phi}$ can be assumed to be equal to $R_{2,0}$ (the apparent dynamic molar refraction of the solute at infinite dilution) and V_2^{∞}, respectively. The $R_{2,0}$ value corresponds only to the electronic part of this property because the contributions from the infrared-active modes (vibrational polarizability) are not considered here [4, 8]. In fact, there is sufficient experimental evidence that justifies this assumption, which indicates this contribution is only between 5 and 10% of the electronic component [9]. As a consequence, it is appropriate to calculate this term as $R_{2,0}^{\nu} = 0.10R_{2,0}$.

3 Experimental section

3.1 General considerations

The phenylhydrazone derivatives (TCPH, PCPH and FCPH) used in this work were prepared by free solvent condensation assisted by microwave irradiation of phenylhydrazine with the appropriate carboxaldehydes, following the methods developed by our group [10].

3.1.1 Experimental determination of the partial molar volumes at infinite dilution

For the determination of the volumetric quantities, the densities of solutions, ρ, as well as the density of solvent, ρ_1, were measured at 293.15 K using a variable-temperature Anton Parr DMA-5000 densitometer that was calibrated before each series of measurements with bi-distilled/degassed water and dry air, with their densities taken from the literature [4, 11]. Additionally, benzene (>99.8%, Merck, spectroscopic grade) was used as a test liquid and the density measured in this work (0.878914 g·cm^{-3}) shows excellent concordance with published data (0.879000, 0.878800 and 0.878660 g·cm^{-3}) [12]. Each density value was determined by measuring the period of oscillation of a vibrating sample cell with a sample volume of 1 mL. The concentration range used was 1.09×10^{-3} to 67×10^{-3} mol·dm^{-3} in all cases. Although, the solvent acetonitrile is known to be a good coordinating compound, a highly dipolar solvent, and weak hydrogen-bond acceptors and donors [4, 13], this dilute range was chosen to avoid experimental problems (precipitation) associated with the low solubility of these materials in this aprotic solvent. For acetonitrile (>99.9%, Merck, spectroscopic grade), the determined value of density ρ_1 (0.782011 g·cm^{-3}) at 293.15 K in this work was found to agree with values previously reported in the literature (0.782000, 0.781983, 0.782100 g·cm^{-3}) [4, 13f,g]. Differences of 5×10^{-6} g·cm^{-3} (TCPH), 8×10^{-6} g·cm^{-3} (FCPH) and 3×10^{-6} g·cm^{-3} (PCPH) were observed between the values of the experimental densities, ρ, of the solutions compared with the values of density ρ^T calculated as $\rho^T = \rho_0 + A(Q^2 - Q_0^2)$, where ρ_0 is the acetonitrile density; Q and Q_0 are the periods of oscillation of solution and acetonitrile, respectively; and A is an empirical constant determined by measurements of the periods of oscillations of pure water and air. Each reported value is an average of five measurements. The reproducibility of each measurement was within $\pm 3 \times 10^{-6}$ g·cm^{-3}. Apparent molar volumes, $V_{2,\phi}$, of each synthesized compound were calculated from the measured densities of the dilute solutions using Eq. (1). The limiting partial molar volumes, V_2^{∞}, of the solutes were determined from the following two procedures: 1) as the average value of $V_{2,\phi}$ determined within the investigated concentration range, and 2) from Eq. (2) using the method of least squares. A comparative analysis between these experimental results was also performed in this work. The partial molecular volumes at infinite dilution for each solute were estimated by the equation $\upsilon_2^{\infty} = V_2^{\infty}/N_A$.

3.1.2 Experimental determination of the apparent molar refraction at infinite dilution

Refractive indexes of both the solvent and solutions were measured with a Bellingham and Stanley High Accuracy ABBE Refractometer 60/LR with a CCD camera at 293.15 K. Because the lowest absorption of each compound occurs at about 470 nm, a sodium ($\lambda =$ 589.3 nm, line D) lamp was employed in our experiments. The concentration range used for these experiments was 1.09×10^{-3} to 67×10^{-3} mol·dm^{-3} in all cases. For acetonitrile, the value of n_1 (1.343695) agreed with values previously reported in the literature (1.343688) [4]. Therefore, the value used here for the $\left(\frac{n_1^2-1}{n_1^2+2}\right)$ term in the Eq. (3) was 0.211671. The procedure followed allowed us to determine that the reproducibility of the experimental refraction index values is better than $\pm 1.5 \times 10^{-5}$. The determination of the dynamic apparent molar refraction, $R_{2,0}$, of each solute at infinite dilution in acetonitrile was carried out within the Kohner-Geffcken-Grunwald-Haley approximation, Eq. (3) [5]. The corresponding electronic and vibrational components of the dynamic apparent molar mean polarizability of each solute were derived from $R_{2,0}$ by means of Eqs. (4) and (5), respectively [14],

$$\bar{\alpha}_m^e = N_A \bar{\alpha}^e = \left(\frac{3}{4\pi}\right) R_{2,0} \tag{4}$$

$$\bar{\alpha}_m^v = N_A \bar{\alpha}^v = \left(\frac{3}{4\pi}\right) (0.1) R_{2,0} \tag{5}$$

where N_A is Avogrado's number, $\bar{\alpha}^e$ and $\bar{\alpha}^v$ are the dynamic molecular mean electronic and vibrational polarizabilities, $\bar{\alpha}_m^e$ and $\bar{\alpha}_m^v$ are dynamic molar electronic and vibrational polarizabilities of the solutes, respectively. Finally, the total molar polarizability of each solute was estimated as being $\bar{\alpha}_m^{e+v} = \bar{\alpha}_m^e + \bar{\alpha}_m^v$. The analyses of the experimental data were performed using the Microcal$^{\text{TM}}$ Origin software package.

3.1.3 Theoretical determination of the molar volume and electronic molar polarizability

The molecular geometries of TCPH, PCPH and FCPH were fully optimized under the constrained C_s symmetry by using gradient techniques with the density functional theory (DFT), using the B3LYP method and the 6−311++G(3d,3p) basis set. Numeric B3LYP methods were employed to calculate the static electronic dipole polarizability, $\bar{\alpha}_T^e$. It is important to note that the B3LYP DFT function is able to account accurately for the exchange and electron correlation effects in the static mean molecular polarizability and molecular geometries [4]. In fact, the geometric parameters obtained in this work for TCPH show excellent concordance with the experimental data available in the literature for the thiophene phenylhydrazone analog (see Table S1 of the supplementary data). The electronic mean molar polarizability was estimated as being $\bar{\alpha}_{T,m}^e = N_A \bar{\alpha}_T^e$. All calculations were carried out using the Gaussian 2003 quantum chemistry package in a PCX86 under Linux [15a]. The molecular volumes for the TCPH, PCPH and FCPH compounds in the gas phase, $V_{T,m}$, were calculated using fully optimized geometries at the B3LYP/6−311++G(3d,3p) level with the Monte-Carlo integration method as implemented in this program. This method estimates the greatest dimension of the molecule based on tabulated values of atomic radii (*e,g*., van der Waals radii) scaled up by 20%.

First, select a rectangular box that encloses the greatest dimension of the molecule. Calculate the electron density of the outer surface of the box. Then revise this calculation if the estimated electron densities of the grid points are greater than the threshold criterion (0.001 au, 1 au $= 6.748$ e·Å^{-3}) and increase the size of the box, and again compute the electron density of the outer surface of the box if any of the grid points have an electron density greater than 0.001 au. Then calculate the volume of the box (V_{box}) and generate N independent random points inside the box, based on the number of points per unit volume. And then, evaluate the electron density of the sample points. Calculate the number of "hits" (N_{occ}) with electron densities greater than 0.001 au. Finally, calculate the molecular volume using the equation $V_{2m}^{T} = \left(\frac{V_{\text{box}}^{*} N_{\text{OCC}}}{N}\right)$ [15b].

4 Results and discussion

The measured densities, ρ, of the solutions in acetonitrile at 293.15 K are presented in Table 1. These data were used in conjunction with Eq. (1) to yield the corresponding apparent molar volume, $V_{2,\phi}$, at a molarity of C. Table 1 reports the experimental $V_{2,\phi}$ values obtained for the examined solutions. The $V_{2,\phi}$ values are shown in Fig. 2 as a function of the molarity of the solutions. Because the solutions used in our study were extremely dilute, in all cases considered the obtained $V_{2,\phi}$ values were practically constant (99% confidence interval) over the examined concentration range. The limiting partial molar volumes V_2^{∞} calculated as the average of the $V_{2,\phi}$ values (method 1) showed excellent agreement (within experimental error) with the V_2^{∞} values obtained by the least-square fitting method based on Eq. (2) (method 2), and the results are also shown in Table 1. It is very important to note that these experimental results suggest that the TCPH, FCPH and PCPH molecules have very low tendencies to form dipolar clusters by self-association in the acetonitrile solvent and thus the microenvironment of each solute in this solvent remains constant through the concentration range studied. In contrast, the acetone phenylhydrazone derivative showed significant self-association by intermolecular hydrogen bonding of the NH proton to the iminic nitrogen in solvents of low polarity [16]. However, in a solvent such as acetonitrile that is known to be a weak hydrogen-bond donor and have a large dipole moment, solute-solvent interactions (dipole-dipole and induced dipole-dipole interactions) appear to become relevant and compete efficiently with the self-association of TCPH, FCPH and PCPH molecules. As a consequence, solute-solute interactions are minimized in the very dilute region studied here. On the other hand, their low solubility in solvents of low polarity means that the attractive forces between solute molecules are more effective in these cases than the solute-solvent induced dipole-dipole and dispersion interactions.

As seen from the data given in Table 1, the V_2^{∞} values follow the following decreasing order: TCPH > PCPH > FCPH. It is noteworthy that the partial molar volume decreases with increasing Pauling electronegativity [17] of the heteroatom of the five-membered heterocyclic ring in the respective solute and with decreasing functional group contribution to the van der Waals molar volume $\{$S(10.8 cm^3·mol^{-1}), N-H(8.08 cm^3·mol^{-1}) and O(5.20 cm^3·mol^{-1})$\}$

Table 1 Measured values of the TCPH-, PCPH- and FCPH-acetonitrile solutions: concentration (C), density (ρ), partial molar volume ($V_{2,\phi}$), refractive index (n), refraction relative per cm^3 (θ), limiting partial molar volume (V_2^∞) and limiting partial molar refraction ($R_{2,0}$) at 293.15 K

$10^3 \times C/\mathrm{mol{\cdot}dm^{-3}}$	$\rho/\mathrm{g{\cdot}cm^{-3}}$	$V_{2,\phi}/\mathrm{cm^3{\cdot}mol^{-1}}$[a]	n	θ
TCPH				
2.24	0.782173	165.83	1.343828	0.074042
3.59	0.782270	166.05	1.343908	0.118578
4.90	0.782365	165.92	1.343999	0.169238
16.00	0.783168	165.84	1.344648	0.530539
32.00	0.784326	165.80	1.345599	1.059966
55.01	0.785990	165.80	1.346969	1.822651
67.40	0.786888	165.78	1.347707	2.233499
	$V_2^\infty = 165.86 \pm 0.10\,\mathrm{cm^3{\cdot}mol^{-1}}$[b]			$\Omega_2 = 33.1035\,\mathrm{cm^3{\cdot}mol^{-1}}$
	$V_2^\infty = 165.78 \pm 0.01\,\mathrm{cm^3{\cdot}mol^{-1}}$[c]		$\alpha^e = 2.704 \times 10^{-23}\,\mathrm{cm^3}$[d]	$\mathrm{R}_{2,0} = 68.21 \pm 0.05\,\mathrm{cm^3{\cdot}mol^{-1}}$
PCPH				
1.09	0.782078	158.10	1.343761	0.036743
2.24	0.782149	157.71	1.343830	0.075155
3.35	0.782218	157.47	1.343897	0.112454
4.49	0.782288	157.62	1.343966	0.150867
16.38	0.783024	157.48	1.344684	0.550581
33.57	0.784088	157.45	1.345723	1.128997
50.27	0.785121	157.46	1.346761	1.706856
67.30	0.786175	157.45	1.347760	2.263004
	$V_2^\infty = 157.60 \pm 0.24\,\mathrm{cm^3{\cdot}mol^{-1}}$[b]			$\Omega_2 = 33.7304\,\mathrm{cm^3{\cdot}mol^{-1}}$
	$V_2^\infty = 157.44 \pm 0.01\,\mathrm{cm^3{\cdot}mol^{-1}}$[c]		$\alpha^e = 2.660 \times 10^{-23}\,\mathrm{cm^3}$[d]	$R_{2,0} = 67.09 \pm 0.03\,\mathrm{cm^3\text{-}mol^{-1}}$
FCPH				
1.09	0.782083	153.38	1.343751	0.031175
2.28	0.782162	153.16	1.343811	0.064578
3.40	0.782236	153.22	1.343869	0.096867
4.60	0.782315	153.34	1.343930	0.130826
17.00	0.783138	153.07	1.344564	0.483776
33.00	0.784199	153.06	1.345381	0.938604
50.30	0.785346	153.06	1.346265	1.430731
70.30	0.786272	153.06	1.347287	1.999863
	$V_2^\infty = 153.17 \pm 0.13\,\mathrm{cm^3{\cdot}mol^{-1}}$[b]			$\Omega_2 = 28.4441\,\mathrm{cm^3{\cdot}mol^{-1}}$
	$V_2^\infty = 153.16 \pm 0.12\,\mathrm{cm^3{\cdot}mol^{-1}}$[c]		$\alpha^e = 2.413 \times 10^{-23}\,\mathrm{cm^3}$[d]	$R_{2,0} = 60.87 \pm 0.08\,\mathrm{cm^3{\cdot}mol^{-1}}$

[a] Determined using Eq. (1).

[b] Estimated as $\bar{V}_2^\infty = \frac{\sum_{i=1}^{n} (V_{2,\phi})_i}{n} \pm \sigma$ (method 1).

[c] Determined using Eq. (2) (method 2).

[d] The estimated random errors in this property lie beyond the last digit quoted.

[18]. On the basis of these observations, and considering that the phenylhydrazonyl unit is present in all molecular systems studied here, it is possible to argue that the intrinsic electronic and volumetric properties of each heteroatom in the respective heterocyclic moiety play fundamental roles in the local organization of the solvent around the solute molecules.

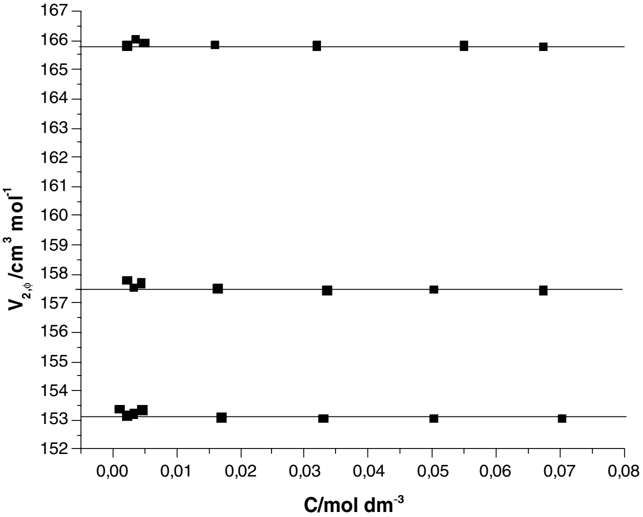


Fig. 2 The apparent molar volumes $V_{2,\phi}$ of the FCPH (▲), PCPH (•) and TCPH (■) compounds *versus* the concentration in acetonitrile at 293.15 K

With the purpose of obtaining additional information on changes in the electronic environment experienced by solutes as the solution becomes more concentrated, we decided to carry out the experimental determination of the apparent electronic molar refraction $R_{2,0}$ of the TCPH, FCPH and PCPH compounds, in acetonitrile as the solvent, in the extremely dilute region. This was done by measuring the refractive index values of both solutions, n, and solvent, n_1, at 293.15 K, using the Na D line (589.3 nm) and High Accuracy Refractometry (HAR) [4] and by using the Kohner-Geffcken-Grunwald-Haley approach [5]. However, prior to the refractometric measurements, the molecular interactions in solution were assessed using UV-vis spectroscopy following the procedure proposed by Lee and coworkers [19]. It was found for each system (see Figs. S2–S4 of the supplementary data) that the lowest wavelength absorption occurs at about 430 nm without an absorption shoulder and that an excellent linear correlation occurs between the absorbance and concentration for the first excited singlet of the solute. This information coupled with the absence of a discernible change in band shape suggest that a constant electronic environment (cybotatic region) occurs for solute molecules over the concentration range studied here. This finding is consistent with the volumetric and refractometric results (see below).

Based on these results, we carried out the experimental determination of the apparent molar refraction of the TCPH, FCPH and PCPH compounds in an off-resonance region in acetonitrile. The excellent linearity (coefficient correlation, $r^2 \approx 1$) in the refractometric data (θ *versus* C plots) also indicates that no changes occur in the solute-solvent interactions over the concentration range studied and therefore the electronic molecular polarizations are additive in all cases. Thus, the concentration-dependent experimental results of the relevant terms of Eq. (3) and the corresponding apparent dynamic electronic molar refraction, $R_{2,0}$, of the TCPH, FCPH and PCPH compounds, are reported in Table 1. As can be seen in this table, the dynamic value of the apparent molar refraction at 589.3 nm determined for these solutes follows the same trend as observed for the partial molar volume at infinite dilution, *i.e.*, the apparent molar refraction decreases with decreasing partial molar volume at infinite dilution.

The corresponding electronic, $\bar{\alpha}_m^e$, and vibrational, $\bar{\alpha}_m^v$, components of the molar mean polarizabilities deduced from Eqs. (4) and (5) were estimated as being (for $\bar{\alpha}_m^e$) 16.28 $cm^3 \cdot mol^{-1}$ (TCPH), 15.98 $cm^3 \cdot mol^{-1}$ (PCPH), 14.52 $cm^3 \cdot mol^{-1}$ (FCPH), and (for $\bar{\alpha}_m^v$) 1.63 $cm^3 \cdot mol^{-1}$ (TCPH), 1.60 $cm^3 \cdot mol^{-1}$ (PCPH), 1.45 $cm^3 \cdot mol^{-1}$ (FCPH), respectively. Therefore, the value of total molar mean polarizability $\bar{\alpha}_m^{e+v}$ for each compound is 17.95 $cm^3 \cdot mol^{-1}$ (TCPH), 17.58 $cm^3 \cdot mol^{-1}$ (PCPH) and 15.97 $cm^3 \cdot mol^{-1}$ (FCPH). In this context, the static electronic molar polarizabilities, $\bar{\alpha}_{T,m}^e$, determined theoretically at the DFT level in this work for TCPH (18.29 $cm^3 \cdot mol^{-1}$), PCPH (17.27 $cm^3 \cdot mol^{-1}$) and FCPH (16.88 $cm^3 \cdot mol^{-1}$) in the gas phase, are higher than our apparent electronic molar polarizabilities, $\bar{\alpha}_m^e$, in acetonitrile. The differences are mainly due to the dielectric solvent effects not considered in the calculations. In fact, the values of molar electronic polarizability for TCPH (14.21 $cm^3 \cdot mol^{-1}$), PCPH (13.45 $cm^3 \cdot mol^{-1}$) and FCPH (12.76 $cm^3 \cdot mol^{-1}$), as estimated using the optimized atomic hybrid polarizabilities method proposed by Miller [20], give a deviation of about 11.5% when compared with the experimental data. Similar differences were obtained by using the empirical method proposed by Vogel [21]. This difference could be the result of solvent-solute interactions. However, the theoretical trends reproduce the experimentally observed trend: TCPH > PCPH > FCPH. It is noteworthy that the theoretical and experimental tendencies for the electronic polarizability of these phenylhydrazone derivatives follow the same order as the electronic polarizability and aromaticity reported previously for heteroaromatic rings (thiophene > pyrrole > furan) and electronegativity of the heteroatom [17]. At this point, it is important to mention that Lazzaretti and Tossell [17a] and Soscún and Hinchliffe [17b] proposed that the electronic polarizability is both an index of aromaticity and a measure of electron delocalization for thiophene, pyrrole and furan compounds. Then, the differences in molar refraction for these phenylhydrazone derivatives in acetonitrile solvent can be related to aromaticity and electronegativity differences among the thiophene, pyrrole and furan moieties.

From of the volumetric, refractometric and spectroscopic results obtained here for the TCPH, PCPH and FCPH compounds, it is reasonable to believe that the solute molecules are isolated in the observed concentration range. In fact, a comparison of the experimental values of the partial molecular volumes at infinite dilution, v_2^∞ (2.77×10^{-22}, 2.61×10^{-22}, and 2.54×10^{-22} $cm^3 \cdot molecule^{-1}$ for TCPH, PCPH and FCPH, respectively), with respect to our theoretical values for the molecular volumes, V_2^T, estimated at the level B3LYP/6−311++G(3d,3p) (2.59×10^{-22} (TCPH), 2.46×10^{-22} (PCPH) and 2.26×10^{-22} $cm^3 \cdot molecule^{-1}$ (FCPH)), gives a variation of 7%, 6.1% and 12%, respectively. Then, on the basis of these results and the solvation model proposed by Terasawa *et al.* [22], it is possible to also argue that the volumetric contribution from solute-solvent interactions to the molar volumes at infinite dilution is very small in each case and that solute molecules are isolated in this medium.

5 Conclusions

The experimental and theoretical results point out, in fact, that the phenylhydrazone derivates of 2-carboxaldehyde thiophene (TCPH), pyrrole (PCPH) and furan (FCPH) do not form stable complexes with the solvent acetonitrile and do not exhibit significant solute-solute association, and that the volumetric contribution from solute-solvent interactions to the partial molar volume is negligible within the studied concentration range. The order of the partial molar volume, V_2^∞, and the apparent molar refraction, $R_{2,0}$, at infinite dilution of these compounds in acetonitrile at 293.15 K (TCPH > PCPH > FCPH) is parallel to the order of the aromaticity of the five-membered heterocyclics (thiophene > pyrrole > furan), the heteroatom volumetric contribution to the van der Waals molar volume and the Pauling electronegativity of the heteroatom.

Acknowledgments

The authors thank the Fondo Nacional de Ciencia, Tecnología e Innovación (FONACIT-Venezuela, Proyect: Apoyo a Grupos No. G-2005000403) and the Consejo de Desarrollo Científico y Humanístico (CONDES-LUZ) for partial financial support of this work and the CeCalcULA (Centro Nacional de Cálculo Científco de la Universidad de los Andes, Mérida-Venezuela). We also are grateful to the referees for providing valuable suggestions and helpful comments concerning this work.

Electronic supplementary material

Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s10953-006-9093-2 and is accessible for authorized users.

References

1. a) Lewis, M., Barrer, C., Hathaway, B., Glaser, R.: 4-Methoxybenzaldehyde pentafluorophenylmethylindenehydarzone. Acta Cryst. **C55**, 975–978 (1999); b) Serbutoviez, C., Bosshard, C., Knöpfle, G., Wyss, P., Prêtre, P., Gunter, P., Schenk, K., Solari, E., Chapuis, G.: Hydrazone derivatives, an efficient class of crystalline materials for nonlinear optics. Chem. Mater. **7**, 1198–1206 (1995); c) Follonier, S., Bosshard, C., Meier, U., Knöpfle, G., Serbutoviez, C., Pan, F., Günter, P.: New nonlinear organic crystal: 4-dimethyl-aminobenzaldehyde-4-nitrophenyl-hydrazone. J. Opt. Soc. Am. **14**, 593–600 (1997); d) Wong, M., Gramlich, V., Pan, F., Bosshard, C., Günter, P.: 5-Mehylthiophene-2-carboxaldehyde-water(1/1). Acta Cryst. **C53**, 757–759 (1997).
2. a) Galey, J., Bombard, S., Chopard, C., Girerd, J., Lederer, F., Thang, D., Nam, N., Mansuy, D., Chottard, J.: Hexanal phenylhydrazone is a mechanism-based inactivator of soybean lipoxygenase 1. Biochem. **27**, 1058–1066 (1988); b) Mahy, J., Gaspard, S., Mansuy, D.: Phenylhydrazone as new good substrates for the dioxygenase and peroxidase reactions of prostaglandin synthase: formation of iron(III)-σ-phenyl complexes. Biochem. **32**, 4104–4021 (1993); c) Mague, J., Vang, S., Berge, D., Wacholtz, W.: Isomerism/tautomerism in hydrazones derived from thiophenaldehydes and 2-hydrazoquinoline. Acta Cryst, **C53**, 973–979 (1997); d) Ding, W., Jiang, X.: Correlation analysis of UV spectral data of some phenylhydrazones and semicarbazones by the dual-parameter equation. Observation of three types of behaviors of the λ_{max} values induced by the polar effects of subtituents. J. Phys. Org. Chem. **11**, 809–818 (1998); e) Pan, F., Wong, M., Bösch, M., Bosshard, C., Meier, U., Günter, P.: A highly efficient organic second-order nonlinear optical crystal based on donor-acceptor substituted 4-nitrophenylhydarzone. Appl. Phys. Lett. **71**, 2064–2066 (1997); f) Thami, T., Bassoul, P., Petit, M., Simon, J., Fort, A., Barzoukas, M., Villaeys, A.: Highly polarizable metallic complexes for nonlinear optics. Cobaltous complexes of unsymmetrical hydrazone imine glyoxal derivatives. J. Am. Chem. Soc. **114**, 915–921 (1992).
3. a) Moscovici, R., Ferraz, J., Neves, E., Tognoli, J., Seoud, M. do Amaral, L.: Mechanism and catalysis for phenylhydrazone formation from aromatic heterocyclic aldehydes. J. Org. Chem. **41**, 4093–4096 (1976); b) Amaral, L.: Mechanism and catalysis for furfural phenylhydrazone formation. J. Org. Chem. **37**, 1433–1436 (1972); c) Westerman, P., Botto, R., Boberts J.: Substituent and medium effects on nitrogen-15 shielding of compounds with >C=N bonds (imines, oximes, and phenylhydrazones). J. Org. Chem. **43**, 2590–2596 (1978); d) Pacansky, J., McLean, A.D., Miller, M.D.: Theoretical calculations and experimental studies on the electronic structures of hydrazones and hydrazone radical cations: formaldehyde hydrazone and benzaldehyde diphenylhydrazones. J. Phys. Chem. **94**, 90–98 (1990).
4. a) Soscún, H., Alvarado, Y., Hernández, J., Hernández, P., Atencio, R., Hinchliffe, A.: Experimental and theoretical determination of the dipole polarizability of dibenzothbiophene. J. Phys. Org. Chem.

14, 709–715 (2001); b) Alvarado, Y.J., Cubillán, N., Labarca, P.H., Karma, A., Arrieta, F., Castellano, O., Soscún, H.: Static and dynamic dipole polarizabilities of 2- and 3-methylthiophene in solution: experimental and theoretical determination. J. Phys. Org. Chem. **15**, 154–164 (2002); c) Alvarado, Y.J., Soscún, H., Velazco. W., Labarca, P.H., Cubillán, N., Hernandez, J.: Dipole polarizability of the pyrazabole molecule in solution. J. Phys. Org. Chem. **15**, 835–843 (2002); d) Alvarado, Y.J., Labarca, P.H., Cubillán, N., Osorio, E., Karam, A.: Solvent effect on electronic polarizability of benzonitrile. Z. Naturforsch. **58a**, 68–74 (2003); e) Alvarado, Y.J., Peña-Suárez, J.L., Cubillán, N., Labarca, P.H., Caldera-Luzardo, J.A., López-Linares, F.: Influence of the dielectric medium on the carbonyl infrared absorption peak of acetylferrocene. Molecules **10**, 457–474 (2005); f) Alvarado, Y.J., Caldera-Luzardo, J., De La Cruz, C., Ferrer-Amado, G., Michelena, E., Silva, P.: Volumetric, electric, and magnetic properties of thioxanthen-9-one in aprotic solvents as revealed by high-precision densitometry, high-accuracy refractometry and magnetic susceptibility measurements and by DFT calculations. J. Solution Chem. **35**, 29–49 (2006); g) Soscun, H., Hernández, J., Escobar, R., Toro-Mendoza, C., Alvarado, Y., Hinchliffe, A.: Ab-initio and density functional theory calculations of the dipole polarizability and the second dipole hyperpolarizability of benzene. Int. J. Quant. Chem. **90**, 497–506 (2002).

5. a) Kohner, H.: Über die Konzentrationsabhängigkeit der Äquivalentrefraktion von starken Elektrolyten in Lösung. Z. Phys Chem. **B1**, 427–455 (1928); b) Geffcken, W.: Über die Konzentrationsabhängigkeit der Äquivalentrefraktion von starken Elektrolyten in Lösung. Z. Phys Chem. **B5**, 81–123 (1929); (c) Grunwald, E., Haley, J.; Acid dissociation constants of trifluoroacetic acid in water measured by differential refractometry. J. Phys. Chem. **72**, 1944–1948 (1968).
6. a) Sakuray, M.: Partial volumes in aqueous mixtures of nonelectrolytic. IV. Aromatic hydrocarbons. Bull. Chem. Soc. Jpn. **63**, 1695–1699 (1990); b) For the extremally dilute regime, Eq. (2) also can be deduced from an expansion in Taylor series of the density, see: Petty, H.R., Crumb, J.A., Anderson, V.E., Arakawa, E.T., Baird, J.K.: New differential Bottcher-Onsager method used to determine polarizability and apparent radius of $SiO_4(WO_3)_{12}^{4-}$. J. Phys. Chem. **81**, 696–703 (1977).
7. a) Mizyed, S., Tremaine, P. Georghiou, P.: Partial molar volumes study of the complexes of calix[4]naphthalenes with [60]fullerene in different solvents. J. Chem. Soc. Perkin Trans. **2**, 3–6 (2001); b) Bernazzani, L., Mollica, V., Tiné, M.: Partial volumes of organic compounds in C8 solvents at 298.15 K. Fluid Phase Equilib. **203**, 15–29 (2002).
8. a) Hohm, U., Goebel, D., Grimme, S.: Experimental study of the dipole polarizability of ferrocene $Fe(C_5H_5)_2$. Chem. Phys. Lett. **272,** 328–334 (1997); b) Brocos, P., Piñero, A., Bravo, R., Amigo, A.: Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations. Phys. Chem. Chem. Phy. **5**, 550–557 (2003).
9. a) Calderbank, K., Calvert, R., Lukins, P., Ritchie, G.: Magnetic anisotropies and relatives aromaticities of pyrrole, pyrazole, imidazole and their N-methyl derivatives. Aust. J. Chem. **34**, 1835–1844 (1981); b) Gussoni, M., Rui, M., Zerbi, G.: Electronic and relaxation contribution to linear molecular polarizability. An analysis of the experimental values. J. Mol. Struct. **447**, 163–214 (1998).
10. Manuscript in preparation.
11. a) Snyder, C., Douglas, J.: Determination of the dielectric constant of nanoparticules. 1. Dielectric measurements of buckminsterfullerene solutions. J. Phys. Chem. B **104**, 11058–11065 (2000); b) Kell, G.S.: Isothermal compressibility of liquid water at 1 atm. J. Chem. Eng. Data. 15, 119–122 (1970).
12. a) Ruelle, P., Farina-Cuendet, A., Kesselring, U.W.: Changes of molar volume from solid to liquid and solution: The particular case of C_{60}. J. Am. Chem. Soc. **118**, 1777–1784 (1996); b) Aminabhavi, T.M., Patel, R.C., Jayadevappa, E.S., Prasad, B.R.: Excess volume and excess polarizability during mixing of binary solvents. J. Chem. Eng. Data. **27**, 50–53 (1982); c) Rudan-Tasic, D., Klofutar, C.: Apparent molar volume and expansibility of cyclohexanol in benzene and cyclohexane. Monasth. Chem. **129**, 1245–1257 (1998).
13. a) Jannell, L., López, A., Saiello, S.: Thermodynamic and physical properties of binary mixture involving sulfolane. Excess volumes and dielectric constants of benzonitrile-sulfolane and acetonitrile-sulfolane systems. J. Chem. Eng. Data **25**, 259–263 (1980); b) Chastrette, M., Rajzmann, M., Chanon, M., Purcell, K.: Approach to a general classification of solvents using a multivariate statistical treatment of quantitative solvent parameters. J. Am. Chem. Soc. **107**, 1–11 (1985); c) Kolling, O., Aprotic solvent effects upon the fundamental vibrational peak of the nitrile group in benzonitrile, Appl. Spectrosc. **54**, 890–893 (2000); d) Abboud, L., Notario, R.: Critical compilation of scales of solvent parameters. Part I. Pure, non-hydrogen bond donor solvents. Pure Appl. Chem. **71**, 645–718 (1999); (e) Fawcett, W., Liu, G., Kessler, T.: Solvent-induced frequency shifts in the infrared spectrum of acetonitrile in organic solvents. J. Chem. Phys. **97**, 9293–9298 (1993); f) Chen Ku, H., Hsiun Tu., C.: Density and viscosity of binary mixtures of propan-2-ol, 1-chlorobutane, and acetonitrile. J. Chem. Eng. Data. **43**, 465–468 (1998); g) Paez, S., Contreras, M.: Densities and viscosities of binary mixtures of 1-propanol with acetonitrile. J. Chem. Eng. Data. **34**, 455–459 (1989).

14. Lopez, R., Monzó, I., Tomas, F.: The apparent dipole moments and molar volumes of 1,3-benzo-thiazole and some derivatives, in nonpolar solvents. J. Chem. Perkin Trans. **2**, 2225–2229 (1999).
15. a) Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, Jr., J.A., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., Pople, J.A.: Gaussian 03, Revision B.02. Gaussian, Inc., Pittsburgh PA (2003); b) Wong, M., Wiberg, K., Frisch. M.: Ab initio calculation of molar volumes: Comparison with experimental and use in solvation models. J. Comp. Chem. **16**, 385–394 (1995).
16. Stassinopoulou, C.I., Petrou, J.: H n.m.r study of the self-association of acetone phenylhydazone by hydrogen bonding. Org. Mag. Resonance. **10**, 79–81 (1977).
17. a) Hinchliffe, A., Soscún, H.: AB initio studies of dipole polarizabilities of conjugated molecules. Part 5. The Five-membered heterocyclics C_4H_4E (E = BH, AlH, CH_2, SiH_2, NH, PH, O and S). J. Mol. Struct. (theochem). **331**, 109–125 (1995); b) Lazzaretti, P., Tossell, J.A.: Coupled Hartree-Fock calculations of the electric dipole polarizability and first hyperpolarizability of some “inorganic benzenes”. J. Mol. Struct. (Theochem) **236**, 403–410 (1991).
18. Bondi, A.: Van der Waals volumes and radii. J. Phys. Chem. **68**, 441–451 (1964).
19. Lee, S., Hotta, S., and Nakanishi, F.: Spectroscopic characteristics and intermolecular interaction of thiophene/phenylene co-oligomers in solutions. J. Phys. A **104**, 1827–1833 (2000).
20. Miller, K.: Additivity methods in molecular polarizability. J. Am. Chem. Soc. **112**, 8533–8542 (1990).
21. Vogel, A.: Physical properties and chemical constitution. Part XXIII. Miscellaneous compounds, investigation of the co-called co-ordinate or dative link in esters of oxy-acids and in nitro-paraffins by molecular refractivity determinations, atomic, structural, and group parachors and refractivities. J. Chem. Soc. 1833–1855 (1948).
22. Terasawa, S., Itsuki, H., Arakawa, S.: Contribution of hydrogen bonds to the partial molar volumes of nonionic solutes in water. J. Phys. Chem. **79**, 2345–2352 (1975).