Solution enthalpies of 1,4-dioxane: Study of solvent effects through quantitative structure–property relationships

Nelson Nunes [a,c,*], Marina Reis [b,c], Luís Moreira [b,c], Ruben Elvas-Leitão [a,c],
Filomena Martins [c]

[a] Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa (ISEL), Instituto Politécnico de Lisboa, Rua Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal
[b] Instituto Superior de Educação e Ciências (ISEC), Alameda das Linhas de Torres, 174, 1750-142 Lisboa, Portugal
[c] 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

ABSTRACT

Solution enthalpies of 1,4-dioxane have been obtained in 15 protic and aprotic solvents at 298.15 K. Breaking the overall process through the use of Solomonov's methodology the cavity term was calculated and interaction enthalpies ($\Delta_{int}H$) were determined. Main factors involved in the interaction enthalpy have been identified and quantified using a QSPR approach based on the TAKA model equation. The relevant descriptors were found to be π^* and β, which showed, respectively, exothermic and endothermic contributions.

The magnitude of $\pi^{*'}$ coefficient points toward non-specific solute–solvent interactions playing a major role in the solution process. The positive value of the β coefficient reflects the endothermic character of the solvents' hydrogen bond acceptor (HBA) basicity contribution, indicating that solvent molecules engaged in hydrogen bonding preferentially interact with each other rather than with 1,4-dioxane.

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1. Introduction

Crown ethers are a group of cyclic molecules with the general formula $(-CH_2CH_2O-)_n$, broadly used in biology, medicine and chemistry. The oxygen atoms present in these molecules are capable of establishing hydrogen bonds with solvent molecules or cations forming complexing agents [1,2]. Several thermochemical studies have been performed using different substrates, 12-crown-4, 15-crown-5 and 18-crown-6 [3–6].

1,4-Dioxane is not classified as a crown ether, however it is the smaller similar cyclic ether and its solution enthalpies have also been extensively studied in aqueous–organic solvent mixtures. The obtained results were discussed in terms of specific hydrogen bonds' influence (anticipating the ability of 1,4-dioxane to act as a lone pair donor and the solvent as a Lewis acid) [5]. Despite all the work done so far, the involved interactions were never properly disclosed.

The aim of this study is to identify how 1,4-dioxane interacts with solvent molecules with different polarities and acid–base properties through a quantitative structure–property relationship (QSPR) methodology.

The solution enthalpy of 1,4-dioxane in any solvent ($\Delta_{sol}H$) can be partitioned into three energetic contributions, due to: (i) the disruption of the solute structure, usually taken as its vaporization enthalpy ($\Delta_{vap}H_{1,4-dioxane} = 35.7$ kJ mol^{-1} [7]), (ii) the creation of a suitable cavity to accommodate the solute, ($\Delta_{cav}H$) and (iii) the breaking of solvent–solvent interactions and formation of new, specific and non-specific, solute–solvent interactions ($\Delta_{int}H$). As so, Eq. (1) can be used to determine the $\Delta_{int}H$ term.

$$\Delta_{int}H = \Delta_{sol}H - \Delta_{cav}H - \Delta_{vap}H \tag{1}$$

The cavity term can be determined, Eq. (2), using Solomonov's reported methodology [8], where $\delta_{cav}h^S$ is the specific relative cavity formation enthalpy for solvent S and V_x is the McGowan characteristic volume ($V_{x\ 1,4-dioxane} = 68.1$ cm^3 mol^{-1}) [9]. In Eq. (2), $\Delta_{cav}H$ represents the difference between the enthalpy of cavity formation in solvent S and a reference solvent which should be a linear alkane with a similar McGowan characteristic volume as that of 1,4-dioxane. Due to this fact, $\Delta_{int}H$ includes also a contribution from the referred enthalpy of cavity formation in the reference solvent.

$$\Delta_{cav}H = \delta_{cav}h^S \cdot V_x \tag{2}$$

* Corresponding author at: Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro, 1, 1959-007 Lisboa, Portugal. Tel.: +351 218317000; fax: +351 218317001.
E-mail address: nnunes@deq.isel.ipl.pt (N. Nunes).

Table 1
Solution enthalpies at 298.15 K and infinite dilution of 1,4-dioxane in several solvents (and associated standard deviations), specific relative cavity formation enthalpy, solute–solvent interaction enthalpy term and Kamlet–Taft solvent descriptors' values.

Solvent	$\Delta_{sol}H \pm s\,\Delta_{sol}H$ (kJ mol^{-1})	$10^2\,\delta_{cav}h^s$ (kJ cm^{-3})	$\Delta_{int}H$ (kJ mol^{-1})	Solvent descriptors [c]		
				π^*	α	β
Cyclohexane	7.50 ± 0.26	1.42[a]	−29.16	0	0	0
Acetonitrile	−0.11 ± 0.01	10.66[a]	−43.07	0.75	0.19	0.37
Dimethylformamide	0.84 ± 0.04	8.62[a]	−40.73	0.88	0	0.69
Dimethylsulfoxide	1.45 ± 0.07	13.87[a]	−43.69	1	0	0.76
Nitromethane	−1.04 ± 0.02	13.74[a]	−46.10	0.85	0.22	0.25
Acetone	0.64 ± 0.01	7.65[a]	−40.27	0.71	0.08	0.48
Propylene carbonate	−0.41 ± 0.01	10.14[a]	−43.02	0.83	0	0.40
Dimethylacetamide	0.57 ± 0.03	7.66[a]	−40.35	0.85[d]	0	0.76
Methanol	4.28 ± 0.07	5.1[b]	−34.90	0.60	0.98[d]	0.73
Ethanol	6.36 ± 0.05	2.8[b]	−31.24	0.55	0.88	0.80
Propan-1-ol	7.71 ± 0.1	1.5[b]	−29.01	0.53	0.79	0.85
Butan-1-ol	7.86 ± 0.17	1.6[b]	−28.93	0.54	0.74	0.84
Propan-2-ol	9.38 ± 0.19	2.8[b]	−28.23	0.48	0.68	0.93
Carbon tetrachloride	−0.55 ± 0.03	1.91[a]	−37.55	0.28	0	0
Ethyl acetate	0.57 ± 0.01	5.98[a]	−39.20	0.55	0	0.45

[a] Ref. [8].
[b] Ref. [17].
[c] Ref. [15].
[d] Ref. [7].

The $\Delta_{int}H$ term can be further evaluated using the well-established Taft–Abboud–Kamlet–Abraham (TAKA) model equation [10], Eq. (3).

$$\Delta_{int}H = a_0 + a_1\pi* + a_2\alpha + a_2\beta \tag{3}$$

In Eq. (3) the descriptors are, π^*-solvent's dipolarity/polarizability; α and β-solvent's hydrogen bond donor (HBD) acidity and hydrogen bond acceptor (HBA) basicity. The a_i values are the complementary solute-dependent coefficients of the solvent parameters.

2. Methodology and results

Following our previous work [11–16], 15 different solvents were chosen taking into consideration the availability of the descriptors, their chemical representativeness and the independency of the chosen scales (the determination coefficient between each pair of descriptors was smaller than 0.5 and for a given descriptor against all others, $R^2 < 0.8$).

Solvents were supplied by Aldrich, Merck and Riedel-de-Haen (min. 99%), with a water content below 0.1% and were used without further drying or purification.

1,4-Dioxane was supplied by Aldrich (min. 99%). Solutes were weighed in a Precisa XT 120A analytical balance with a precision of ±0.1 mg and their concentration ranged from 0.010 to 0.003 mol dm^{-3}.

Solution enthalpies were measured at 298.15 ± 0.01 K using a Thermometric 2225 precision solution calorimeter. This equipment operates under semiadiabatic conditions and has a temperature resolution in the order of 1 μK, corresponding to a resolution in enthalpy of (1–4) mJ. Cylindrical ampoules were filled with solute and sealed. Each sealed ampoule was immersed into 100 mL of solvent, inside the glass reaction vessel, and stirred at (500–600) rpm. Two electrical calibrations were performed before and after breaking each ampoule. Each reported enthalpy value in a given solvent, results from the average of at least three independent experiments, with a relative standard deviation always less than 5%. Heats of empty ampoule breaking, measured in the solvent with the higher vapor pressure (acetone), were found to be negligible [15].

The performance and accuracy of the calorimetric system was tested by measuring the solution enthalpy of

Table 2
Comparison of solution enthalpies at 298.15 K and infinite dilution of 1,4-dioxane between this work and literature values.

Solvent	This work $\Delta_{sol}H$ (kJ mol^{-1})	Lit. $\Delta_{sol}H$ (kJ mol^{-1})
Acetonitrile	−0.11	−0.11[a]
Dimethylformamide	0.84	0.86[b]
Dimethylsulfoxide	1.45	1.65[c], 1.7[d]
Acetone	0.64	0.6[d], 0.74[e]
Propan-1-ol	7.71	7.81[f], 7.65[g]

[a] Ref. [4].
[b] Ref. [3].
[c] Ref. [18].
[d] Ref. [19].
[e] Ref. [20].
[f] Ref. [21].
[g] Ref. [5].

tris(hydroxymethyl)aminomethane (TRIS) in both 0.05 mol dm^{-3} NaOH and 0.1 mol dm^{-3} HCl. Experimental and literature values agree within experimental uncertainty [14].

Table 1 summarizes the obtained solution enthalpies of 1,4-dioxane and associated standard deviations at 298.15 K and infinite dilution; the interaction enthalpy term calculated by Eq. (1), and the descriptors' values of each solvent.

Table 2 compares the solution enthalpies obtained in this work and values already presented in the literature, showing a good agreement between them.

The multiparametric linear regression (MLR) analysis was applied between the $\Delta_{int}H$ term and the set of Kamlet–Taft solvent descriptors (π^*, α and β) leading to Eq. (4). This choice was based on rigorous statistical criteria [22,23] and followed a backward elimination process. The significance level, SL, for each regression coefficient, the standard deviation of the fit, sd_{fit}, the adjusted determination coefficient, R^2_{adj}, and Fisher's F value were computed and analyzed. Internal validation was further assessed by calculating the cross-validation correlation coefficient, Q^2_{LOO} (using the leave-one-out (LOO) approach).

$$\Delta_{int}H = -29.91_{\pm 0.89} \quad -24.70_{\pm 1.37}\ \pi^* + 15.09_{\pm 1.16}\beta$$
$$(100\%) \qquad (100\%) \qquad (100\%)$$
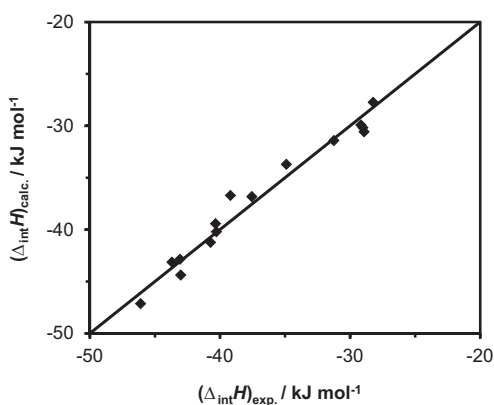$$N = 15,\ R^2_{adj} = 0.962,\ sd_{fit} = 1.204,\ F = 182,\ Q^2_{LOO} = 0.969 \tag{4}$$

Fig. 1. Calculated *vs.* experimental $\Delta_{int}H$ values.

3. Discussion

The plot of calculated *vs.* experimental $\Delta_{int}H$ values (Fig. 1) confirms that there are no outliers (a given point is considered an outlier if $|\Delta_{int}H_{calc} - \Delta_{int}H_{exp}| > 2\ sd_{fit}$) and that Eq. (4) is suitable to describe the solution process of 1,4-dioxane.

The statistical figures of merit (Eq. (4)) show unambiguously the goodness-of-fit. In particular, Q_{LOO}^2 being higher than 0.6, assesses the robustness of the model.

An indirect measure of the quality of the model equation is the simulation of vacuum as solvent medium ($\beta = 0$ and $\pi^* = -1.2$) [7], obtaining in this case $\Delta_{int}H$ close to zero, as expected. This also indicates a very small enthalpy of cavity formation in the reference solvent.

The obtained model equation shows that only π^* and β terms are relevant to explain $\Delta_{int}H$ values. Noticeably, our results indicate that the solvents' hydrogen bond donor (HBD) capacity does not quantitatively influence the solution process of 1,4-dioxane. This can be explained considering that, in the overall process, the necessary energy to break HBD solvent to solvent interactions cancels out the released energy resulting from the establishment of new solvent to solute HBD interactions [24,25]. This also might indicate that the oxygen atoms of 1,4-dioxane are available to act as lone pair donors.

The negative value of the π^* term reveals an exothermic contribution due to the solvents' dipolarity/polarizability ability. The magnitude of the term shows that the non-specific solute–solvent interactions play a major role in the solution process. This might be explained especially by the polarizability of 1,4-dioxane and not so much by its dipolarity.

The positive value of the β term reflects the endothermic character of the solvents' hydrogen bond acceptor (HBA) basicity contribution. The interpretation is that in the overall process, the energy necessary to break HBA solvent–solvent interactions surpasses the released energy resulting from the establishment of new solvent–solute HBA interactions, which due to the absence of acidic centers in 1,4-dioxane can therefore be taken as zero.

Acknowledgment

References

[1] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, Thermodynamic and kinetic data for macrocycle interaction with cations and anions, Chem. Rev. 91 (1991) 1721–2085.

[2] R.M. Izatt, J.S. Bradshaw, K. Pawlak, R.L. Bruening, B.J. Tarbet, Thermodynamic and kinetic data for macrocycle interaction with neutral molecules, Chem. Rev. 92 (1992) 1261–1354.

[3] M. Jóźwiak, Thermochemical behavior of crown ethers in the mixtures of water with organic solvents. Part VIII. Hydrophobic hydration and preferential solvation of 1,4-dioxane in $\{(1 - x)$amide$ + xH_2O\}$ at $T = 298.15$ K, J. Chem. Thermodyn. 39 (2007) 433–437.

[4] M. Jóźwiak, Thermochemical behaviour of crown ethers in the mixtures of water with organic solvents. Part IX. Effect of base–acid properties of $\{(1 - x)$AN$ + xH_2O\}$ on the solution enthalpy of cyclic ethers in this mixed solvent at $T = 298.15$ K, J. Chem. Thermodyn. 41 (2009) 522–524.

[5] M. Jóźwiak, Effect of base–acid properties of the mixture of water with propan-1-ol on the solution enthalpy of cyclic ethers in this mixture at $T = 298.15$ K, J. Chem. Eng. Data 56 (2011) 4710–4714.

[6] M. Jóźwiak, L. Madej-Kielbik, H. Piekarski, Effect of temperature on the solvation of 15-crown-5 ether in water–methanol mixtures, Thermochim. Acta 533 (2012) 22–27.

[7] Y. Marcus, The Properties of Solvents, John Wiley & Sons, New York, 1999.

[8] B.N. Solomonov, V.B. Novikov, M.A. Varfolomeev, N.M. Mileshko, A new method for the extraction of specific interaction enthalpy from the enthalpy of solvation, J. Phys. Org. Chem. 18 (2005) 49–61.

[9] M.H. Abraham, J.C. McGowan, The use of characteristic volumes to measure cavity terms in reversed phase liquid chromatography, Chromatographia 23 (1987) 243–246.

[10] R.W. Taft, J.L.M. Abboud, M.J. Kamlet, M.H. Abraham, Linear solvation energy relations, J. Solution Chem. 14 (1985) 153–186.

[11] F. Martins, N. Nunes, M.L. Moita, R.E. Leitão, Solution enthalpies of 1-bromoadamantane in monoalcohols at 298.15 K, Thermochim. Acta 444 (2006) 83–85.

[12] N. Nunes, F. Martins, R.E. Leitão, Thermochemistry of 1-bromo-adamantane in binary mixtures of water–aprotic solvent, Thermochim. Acta 441 (2006) 27–29.

[13] F. Martins, N. Nunes, L. Moreira, R.E. Leitão, Determination of solvation and specific interaction enthalpies of adamantine derivatives in aprotic solvents, J. Chem. Thermodyn. 39 (2007) 1201–1205.

[14] M. Reis, R.E. Leitão, F. Martins, Enthalpies of solution of 1-butyl-3-methylimidazolium tetrafluoroborate in 15 solvents at 298.15 K, J. Chem. Eng. Data 55 (2010) 616–620.

[15] F. Martins, L. Moreira, N. Nunes, R.E. Leitão, Solvent effects on solution enthalpies of adamantyl derivatives, J. Therm. Anal. Calorim. 100 (2010) 483–491.

[16] M. Reis, L. Moreira, N. Nunes, R. Leitão, F. Martins, Solution enthalpies of hydroxylic compounds study of solvent effects through quantitative structure property relationships, J. Therm. Anal. Calorim. 108 (2012) 761–767.

[17] B.N. Solomonov, V.B. Novikov, M.A. Varfolomeev, A.E. Klimovitskii, Calorimetric determination of hydrogen-bonding enthalpy for neat aliphatic alcohols, J. Phys. Org. Chem. 18 (2005) 1132–1137.

[18] M. Jóźwiak, The effect of carbonyl carbon atom replacement in acetone molecule (CAN) by sulfur atom (DMSO). The preferential solvation of cyclic ethers, J. Therm. Anal. Calorim. 93 (2008) 701–705.

[19] E. M.Kulikov, O.A. Antonova, E.P. Slyusar, E.P. Korolev, Enthalpies of dissolution of propylene carbonate, acetonitrile, and 1,4-dioxane in mixtures of water with acetone or dimethyl sulfoxide, Russ. Chem. Bull. 44 (1995) 1678–1683.

[20] M. Jóźwiak, The effect of carbonyl carbon atom replacement in acetone molecule (ACN) by sulfur atom (DMSO). Part III. Effect of base–acid properties of the mixtures of water with acetone or dimethylsulfoxide on the solution enthalpy of cyclic ethers in mixed solvent, J. Therm. Anal. Calorim. 101 (2010) 1039–1045.

[21] A.V. Kustov, O.A. Antonova, V.P. Korolev, Enthalpies of 1,4-dioxane, 1,2-dimethoxyethane,and ethylacetate solvation in the water–1-propanol and water–glycerol binary mixtures, J. Solution Chem. 31 (2002) 671–680.

[22] F. Martins, C. Ventura, Application of quantitative structure–activity relationships to the modeling of antitubercular compounds. 1. The hydrazide family, J. Med. Chem. 51 (2008) 612–624.

[23] A. Tropsha, P. Gramatica, V.K. Gombar, The importance of being earnest: validation is the absolute essential for successful application and interpretation of QSPR models, QSAR Comb. Sci. 22 (2003) 69–77.

[24] K.V. Zaitseva, M.A. Varfolomeev, V.B. Novikov, B.N. Solomonov, Enthalpy of cooperative hydrogen bonding in complexes of tertiary amines with aliphatic alcohols: calorimetric study, J. Chem. Thermodyn. 43 (2011) 1083–1090.

[25] K.V. Zaitseva, M.A. Varfolomeev, B.N. Solomonov, Thermodynamics of hydrogen bonding of weak bases in alcohol solutions: calorimetry of solution, IR-spectroscopy and vapor pressure analysis, J. Mol. Struct. 1018 (2012) 14–20.