



# Use of quantitative structure–property relationships to study the solvation process of 18-crown-6



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## ABSTRACT

Solution enthalpies of 18-crown-6 have been obtained for a set of 14 protic and aprotic solvents at 298.15 K. The complementary use of Solomonov's methodology and a QSPR-based approach allowed the identification of the most significant solvent descriptors that model the interaction enthalpy contribution of the solution process ( $\Delta_{\text{int}}H^{A/S}$ ). Results were compared with data previously obtained for 1,4-dioxane. Although the interaction enthalpies of 18-crown-6 correlate well with those of 1,4-dioxane, the magnitude of the most relevant parameters,  $\pi^*$  and  $\beta$ , is almost three times higher for 18-crown-6. This is rationalized in terms of the impact of the solute's volume in the solution processes of both compounds.

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## 1. Introduction

Crown ethers have been the object of considerable scientific interest due to their unique chemical properties, which have been useful, for instance, in phase transfer catalysis [1] or cation complexation [2,3]. Since these processes occur in the liquid phase, several studies have been intended to understand the interactions of crown ethers with solvents [4–7]. These compounds are also part of a much broader class of molecules, that of cyclic ethers. In a previous paper we have discussed the solution enthalpies of one such compounds, viz., 1,4-dioxane [8]. In that work, quantitative structure–property relationships (QSPR) were used to analyze the type and magnitude of solvent effects, thus allowing a deeper and more systematic understanding of the solution process of 1,4-dioxane. We have now extended the same methodology to the study of the crown ether 1,4,7,10,13,16-hexaoxacyclooctadecane, commonly referred as 18-crown-6 (Fig. 1).

Given that 1,4-dioxane and 18-crown-6 share some structural similarities, this study will investigate if they also share similarities

in the corresponding solution processes. Moreover, because 18-crown-6 is much larger than 1,4-dioxane, this work will further analyze the impact of the solute's size on the type and/or magnitude of the various interactions affecting these processes.

A quantitative structure–property relationship (QSPR) approach to solution enthalpies has already been thoroughly applied and discussed by us in previous works [8–11]. In all these studies the Taft–Abboud–Kamlet–Abraham–(TAKA) model equation (Eq. (1)) [12] was used to quantify the dominant specific and non-specific solute–solvent interactions,  $\Delta_{\text{int}}H^{A/S}$ , involved in the solution process.

$$\Delta_{\text{int}}H^{A/S} = a_0 + a_1\pi^* + a_2\alpha + a_3\beta \quad (1)$$

In this equation (Eq. (1))  $\pi^*$  represents the solvents' dipolarity/polarizability and  $\alpha$  and  $\beta$ , the solvents' hydrogen bond donor (HBD) acidity and hydrogen bond acceptor (HBA) basicity, respectively, while A and S stand for solute and solvent. The  $a_i$  values are the complementary solute-dependent coefficients.

Solute–solvent interactions ( $\Delta_{\text{int}}H^{A/S}$ ) can be evaluated through Eq. (2):

$$\Delta_{\text{int}}H^{A/S} = \Delta_{\text{sol}}H^{A/S} - \Delta_{\text{vap/sub}}H^A - \Delta_{\text{cav}}H^{A/S} \quad (2)$$

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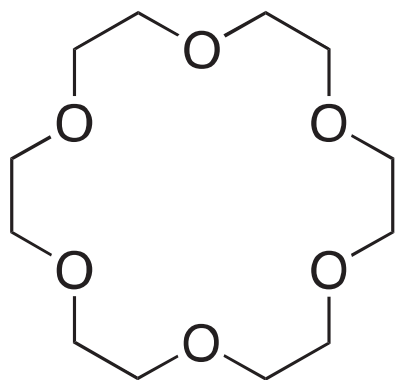


Fig. 1. Structure of 18-crown-6.

where  $\Delta_{\text{sol}}H^{A/S}$  is the solution enthalpy of a given solute A in a solvent S,  $\Delta_{\text{vap/subl}}H^A$  is the solute's vaporization or sublimation enthalpy (depending on the solute's standard state at the working temperature) which is a measure of the solute's structure disruption during the solution process and  $\Delta_{\text{cav}}H^{A/S}$  is the cavity term, which measures the creation of a cavity in the solvent to accommodate the solute, with the corresponding partial breaking of solvent–solvent interactions.

The reported value for the sublimation enthalpy of 18-crown-6 ( $\Delta_{\text{subl}}H_{18\text{-crown-6}}$ ) is  $128.1 \text{ kJ mol}^{-1}$  [13] and the cavity term ( $\Delta_{\text{cav}}H^{A/S}$ ) can be determined using Solomonov's methodology and Eq. (3) [14].

$$\Delta_{\text{cav}}H^{A/S} = \delta_{\text{cav}}h^S \cdot V_x^A \quad (3)$$

In Eq. (3),  $\delta_{\text{cav}}h^S$  is the specific relative cavity formation enthalpy for solvent S and  $V_x^A$  is the McGowan characteristic volume of solute A ( $V_{x18\text{-crown-6}} = 204.3 \text{ cm}^3 \text{ mol}^{-1}$  [15]). In this equation,  $\Delta_{\text{cav}}H^{A/S}$  (and, for that matter,  $\delta_{\text{cav}}h^S$ ) corresponds, in fact, to the difference between  $\Delta_{\text{cav}}H^{A/S}$  in solvent S and a reference solvent which ought to be a linear alkane with a comparable McGowan

characteristic volume, in this case as that of 18-crown-6.  $\Delta_{\text{int}}H^{A/S}$  comprises, therefore, also a contribution from  $\Delta_{\text{cav}}H^{A/S}$  in the reference solvent.

## 2. Experimental

18-Crown-6 in its standard state (i.e., solid) was supplied by Fluka (>99%) and weighed in a Precisa XT 120A analytical balance with a precision of  $\pm 0.1 \text{ mg}$  and its concentration ranged from  $0.006$  to  $0.009 \text{ mol dm}^{-3}$ .

A set of 14 different solvents was chosen based on their chemical representativeness and descriptors availability, guaranteeing at the same time the absence of any intercorrelation among the above referred solvent scales, namely  $\alpha$ ,  $\beta$  and  $\pi^*$  scales [8,16]. Solvents were supplied by Aldrich, Sigma–Aldrich and Panreac (min 99%), with a water mass fraction below 0.1% and were used without further drying or purification. Further details on solute and solvents specifications are presented in Table S1 in Supplementary data.

Solution enthalpies were measured at  $298.15 \pm 0.01 \text{ K}$  using a Thermometric 2225 precision solution calorimeter which has been fully described elsewhere [8,17–19]. All measurements were done at an average pressure of  $1015.2 \pm 0.2 \text{ h Pa}$ .

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 2.1%. Heats of empty ampoule breaking, measured in the solvent with the higher vapor pressure (acetone), were found to be negligible [10].

The performance and accuracy of the calorimetric measurements were tested by determining the solution enthalpy of tris (hydroxymethyl)aminomethane (TRIS) in  $0.05 \text{ mol dm}^{-3}$  NaOH and  $0.1 \text{ mol dm}^{-3}$  HCl [11]. Experimental and literature values [20] agree within experimental uncertainty.

## 3. Results

Average solution enthalpies of 18-crown-6 at  $298.15 \text{ K}$ ,  $1015.2 \text{ h Pa}$  and infinite dilution and respective expanded uncertainties,  $U$ ,

Table 1

Solution enthalpies at  $298.15 \text{ K}$ ,  $1015.2 \text{ h Pa}$  and infinite dilution (and respective expanded uncertainties,  $U$ , at the 0.95 level of confidence), specific relative cavity formation enthalpies and solute–solvent interaction enthalpies for 18-crown-6 (s) in the set of solvents used in this work, and Kamlet–Taft solvent descriptors.<sup>a</sup>

No.	Solvent	$\Delta_{\text{sol}}H^{A/S} \pm U\Delta_{\text{sol}}H^{A/S}/\text{kJ mol}^{-1}$ (this work) <sup>a</sup>	$\Delta_{\text{sol}}H^{A/S}/\text{kJ mol}^{-1}$ (literature)	$10^2\delta_{\text{cav}}h^S/\text{kJ cm}^{-3}$	$\Delta_{\text{int}}H^{A/S}/\text{kJ mol}^{-1}$	Solvent descriptors <sup>d</sup>		
						$\pi^*$	$\alpha$	$\beta$
1	Cyclohexane	$49.44 \pm 1.16$	–	$1.42^g$	–81.56	0	0	0
2	Dimethylformamide	$33.76 \pm 0.38$	$34.7^a$ ; $34.81^b$	$8.62^g$	–111.95	0.88	0	0.69
3	Dimethylsulfoxide	$28.67 \pm 0.09$	$29.3^a$ ; $27.62^b$	$13.87^g$	–127.77	1	0	0.76
4	Acetone	$36.76 \pm 0.34$	$41^c$	$7.65^g$	–106.97	0.71	0.08	0.48
5	Propylene carbonate	$24.78 \pm 1.29$	$24.3^a$	$10.14^g$	–124.04	0.83	0	0.40
6	Dimethylacetamide	$37.00 \pm 0.19$	–	$7.66^g$	–106.75	0.85	0	0.76
7	Methanol	$35.13 \pm 0.97$	$34.70^d$	$5.1^h$	–103.39	0.60	0.98	0.73
8	Ethanol	$43.11 \pm 0.26$	–	$2.8^h$	–90.71	0.55	0.88	0.80
9	Propan-1-ol	$45.97 \pm 0.19$	$45.5^e$	$1.5^h$	–85.19	0.53	0.79	0.85
10	Butan-1-ol	$44.77 \pm 0.95$	–	$1.6^h$	–86.60	0.54	0.74	0.84
11	Propan-2-ol	$46.70 \pm 1.58$	–	$2.8^h$	–87.12	0.48	0.68	0.93
12	Carbon tetrachloride	$32.63 \pm 0.55$	$32.4^f$	$1.91^g$	–99.37	0.28	0	0
13	Ethyl acetate	$34.57 \pm 0.54$	–	$5.98^g$	–105.75	0.55	0	0.45
14	1,4-dioxane	$36.10 \pm 0.25$	–	$7.57^g$	–107.46	$0.49^i$	$0^j$	$0.37^j$

<sup>a</sup> Ref. [5].

<sup>b</sup> Ref. [4].

<sup>c</sup> Ref. [21].

<sup>d</sup> Ref. [22].

<sup>e</sup> Ref. [6].

<sup>f</sup> Ref. [23].

<sup>g</sup> Ref. [14].

<sup>h</sup> Ref. [24].

<sup>i</sup> Ref. [8].

<sup>j</sup> Ref. [15].

<sup>\*</sup> Standard uncertainties  $u$  are  $u(T) = 0.01 \text{ K}$ ,  $u(p) = 0.2 \text{ h Pa}$  and  $u(m) = 0.1 \text{ mg}$ .

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