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Correlation of enthalpic and volume characteristics of 15-crown-5 in solution with molecular parameters and physical properties of solvents

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Abstract

The solution and solvation enthalpies at infinite dilution of 15-crown-5 in different organic solvents and water were measured. The limiting partial molar volumes of the crown ether in a series of solvents studied were determined using experimental density data. On the basis of the scaled particle theory the satisfactory multiparameter correlation of the quantities measured with properties of solvents was obtained. The known equations as modified by the introduction of more accurate radial distribution function $g_{12}(r)$ were used. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The establishment of the patterns of change of summary thermodynamic characteristics of nonelectrolytes in solution depending on the nature of the solvent may be carried out by means of their division into contributions according to the scaled particle theory [1]. The following contributions may be distinguished for standard solvation enthalpies ($\Delta_{\mathrm{solv}}H^0$) and limiting partial molar volumes ($\overline{V}_2^0$)

$$\Delta_{\mathrm{solv}}H^0 = \overline{H}_{\mathrm{cav}} + \overline{H}_{\mathrm{disp}} + \overline{H}_{\mathrm{dd}} + \overline{H}_{\mathrm{ind1}} + \overline{H}_{\mathrm{ind2}} - RT(1-\rho T) \quad (1)$$

$$\overline{V}_2^0 = \overline{V}_{\mathrm{cav}} + \overline{V}_{\mathrm{disp}} + \overline{V}_{\mathrm{dd}} + \overline{V}_{\mathrm{ind1}} + \overline{V}_{\mathrm{ind2}} + \beta RT \quad (2)$$

where index cav is the effect of cavity formation, disp the contribution of solute–solvent dispersion interactions; dd the contribution of dipole–dipole interactions, ind1 and ind2 the effects of polarization of solvent and solute, respectively, ρ the coefficient of thermal expansion of the solvent, and β the isothermal compressibility of solvent.

In order to describe the contributions of intermolecular interactions, the known potentials of pair interactions being averaged over all dipole orientations may be used [1]

$$\langle U_{\mathrm{dd}}\rangle = -\frac{2}{3kT}\frac{\mu_1^2\mu_2^2}{r^6} \quad (3)$$

$$\langle U_{\mathrm{ind1}} + U_{\mathrm{ind2}}\rangle = -\frac{\mu_1^2\alpha_2}{r^6} - \frac{\mu_2^2\alpha_1}{r^6} \quad (4)$$

$$U_{\mathrm{disp}} = 6mc^2\frac{\alpha_1\alpha_2}{\alpha_1/\chi_1 + \alpha_2/\chi_2}\left(\frac{1}{r^6} - \frac{\sigma_{12}^6}{r^{12}}\right) = C_6\left(\frac{1}{r^6} - \frac{\sigma_{12}^6}{r^{12}}\right) \quad (5)$$

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where μ_i is the dipole moment of molecule, α_i the polarizability, χ_i the diamagnetic susceptibility, m the mass of an electron, c the velocity of light in vacuum, σ_{12} the distance of the closest approach of molecules and is equal to half the sum of molecular diameters. The indexes 1 and 2, respectively, relate to solvent and solute characteristics.

The partial free energy of solute – solvent interactions is determined according to

$$\overline{G}_{\mathrm{int}} = \frac{4\pi N^2}{V_1} \int_0^\infty u_{12} g_{12}(r) r^2 \mathrm{d}r \tag{6}$$

where V_1 is the molar volume of the solvent, and $g_{12}(r)$ the radial distribution function. Usually, $g_{12}(r)$ is equated to unity at the distance r ranging from σ_{12} to infinity. It leads to insufficient accuracy in the analysis of solute characteristics in a series of solvents. In this work, we have used a more complicated expression for $g_{12}(r)$, taking into account the increase of density of particles in the first solvation sphere according to Ref. [2]

$$g_{12}(r) = \begin{cases} 0, & r < \sigma_{12} \\ 1 + \frac{4\pi N\sigma_{12}^3}{3V_1}\left[1 - \frac{3r}{4\sigma_{12}} + \frac{1}{16}\left(\frac{r}{\sigma_{12}}\right)^3\right], & \sigma_{12} \le r \le 2\sigma_{12} \\ 1, & r > 2\sigma_{12} \end{cases} \tag{7}$$

Using Eq. (7), the equation for partial characteristics of interaction was obtained as follows:

$$\begin{aligned} \overline{Y}_{\mathrm{int}} = {} & \frac{16\pi N^2 mc^2}{3V_1}\frac{\alpha_1\alpha_2}{\alpha_1/\chi_1 + \alpha_2/\chi_2}\frac{k_1}{\sigma_{12}^3} \\ & - \mu_2^2\left(\frac{8\pi N^2}{3V_1}\frac{\mu_1^2}{3kT}\frac{k_2}{\sigma_{12}^3} + \frac{4\pi N^2}{3V_1}\alpha_1\frac{k_3}{\sigma_{12}^3}\right) \\ & - \frac{4\pi N^2}{3V_1}\mu_1^2\alpha_2\frac{k_4}{\sigma_{12}^3} \end{aligned} \tag{8}$$

The k_i values for free energy of interactions are given as

$$k_1 = 1 + 0.7135\frac{3\pi N\sigma_{12}^3}{8V_1}$$

$$k_2 = k_3 = k_4 \equiv 1 + 0.86\frac{\pi N\sigma_{12}^3}{4V_1}$$

The k_i values for enthalpy and volume effect of interaction were determined using the relations: $\overline{H}_{\mathrm{int}} = \overline{G}_{\mathrm{int}} - T\partial\overline{G}_{\mathrm{int}}/\partial T$ and $\overline{V}_{\mathrm{int}} = \partial\overline{G}_{\mathrm{int}}/\partial P$. So that, for $\overline{H}_{\mathrm{int}}$

$$\left.\begin{aligned} k_1 &= 1 + \rho T + 0.7135\tfrac{3\pi N\sigma_{12}^3}{8V_1}(1 + 2\rho T) \\ k_2 &= 2 + \rho T - \tfrac{T}{\mu_1^2}\tfrac{\partial\mu_1^2}{\partial T} + 0.86\tfrac{\pi N\sigma_{12}^3}{4V_1}\left(2 + 2\rho T - \tfrac{T}{\mu_1^2}\tfrac{\partial\mu_1^2}{\partial T}\right) \\ k_3 &= 1 + \rho T + 0.86\tfrac{\pi N\sigma_{12}^3}{4V_1}(1 + 2\rho T) \\ k_4 &= 1 + \rho T - \tfrac{T}{\mu_1^2}\tfrac{\partial\mu_1^2}{\partial T} + 0.86\tfrac{\pi N\sigma_{12}^3}{4V_1}\left(1 + 2\rho T - \tfrac{T}{\mu_1^2}\tfrac{\partial\mu_1^2}{\partial T}\right) \end{aligned}\right\} \tag{9}$$

and for $\overline{V}_{\mathrm{int}}$

$$\left.\begin{aligned} k_1 &= \beta\left(1 + 0.7135\tfrac{3\pi N\sigma_{12}^3}{4V_1}\right) \\ k_2 = k_3 = k_4 &\equiv \beta\left(1 + 0.86\tfrac{\pi N\sigma_{12}^3}{2V_1}\right) \end{aligned}\right\} \tag{10}$$

The $(T/\mu_1^2)(\partial\mu_1^2/\pi T)$ value is equated to zero in a nonpolar medium. In a polar medium, $(\partial\mu_1^2/\partial T)/\mu_1^2$ may be evaluated from the Debye equation for polarization of dielectrics

$$\begin{aligned} \frac{T}{\mu_1^2}\frac{\partial\mu_1^2}{\partial T} = 1 + {} & \left(1 + \frac{\alpha_1}{\mu_1^2}3kT\right) \\ & \times\left(\rho T + \frac{3T\partial\epsilon/\partial T}{(\epsilon + 1)(\epsilon + 2)}\right) \end{aligned}$$

Eq. (8) cannot describe satisfactorily the contribution of intermolecular interactions in solutions due to the demerits of initial potentials of interactions, the influence of three-dimensional effects in solvation spheres and the deviation of real radial distribution function from spherical symmetry. In the approach suggested by us, Eq. (8) is assumed to approximate correlations for the $\Delta_{\mathrm{solv}}H^0$ and $\overline{V}_2^0$ values determined experimentally. We introduce two coefficients, A_1 and A_2, permitting to use effective constant C_6^{eff} in Eq. (5) and the effective dipole moment of the unperturbed solute molecule μ_2^{eff} in Eqs. (3) and (4): $C_6^{\mathrm{eff}} = A_1 C_6$ and $(\mu_2^{\mathrm{eff}})^2 = A_2\mu_2^2$. The effect of perturbation of the solute molecule is taken into account by inductive contributions. Then, from Eqs. (1), (2) and (8), we can obtain the correlation for solvation enthalpy and limiting partial molar volume of solute with molecular characteristics and physical properties of the solvents:

$$\left.\begin{array}{c}(\Delta_{\mathrm{solv}}H^0-\overline{H}_{\mathrm{cav}}+RT(1-\rho T))\times 10^{10}\\ \overline{V}_2^0-\overline{V}_{\mathrm{cav}}-\beta RT\end{array}\right\}$$

$$=A_1\left(\frac{16\pi N^2mc^2}{3V_1}\frac{\alpha_1\alpha_2}{\alpha_1/\chi_1+\alpha_2/\chi_2}\frac{k_1}{\sigma_{12}^3}\right)-A_2\mu_2^2\left(\frac{8\pi N^2}{3V_1}\frac{\mu_1^2}{3kT}\frac{k_2}{\sigma_{12}^3}+\frac{4\pi N^2}{3V_1}\alpha_1\frac{k_3}{\sigma_{12}^3}\right)-\frac{4\pi N^2}{3V_1}\mu_1^2\alpha_2\frac{k_4}{\sigma_{12}^3} \quad (11)$$

where $\Delta_{\mathrm{solv}}H^0$ are in kJ mol^{-1}; R is in kJ mol^{-1} K^{-1}; βRT and all values in the left part of Eq. (11) are in CGS units. The coefficients k_i are determined according to Eqs. (9) and (10).

In this study, the correlations (Eq. (11)) have been used to analyse the experimental data on enthalpies of solvation and partial molar volumes of 15-crown-5 as conformationally flexible macrocyclic compound [3]. Conformational peculiarities of the solute in a series of solvents must influence the coefficients of correlative relation because the conformers have different molecular forms and dipole moments.

2. Experimental

2.1. Materials

The purity of the 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) studied was 99%. The crown ether was dried by molecular sieves of 0.3 nm size.

The solvents used (carbon tetrachloride, benzene, chloroform, ethylacetate, acetone, pyridine, dimethylformamide, dimethylsulfoxide, acetonitrile) were purified according to standard procedures [4]. All these were dried by molecular sieves. The purity of the solvents was checked by density measurements.

2.2. Calorimetry

Solution enthalpies were measured by means of an isothermal calorimeter at 298.15 K. The vessel was charged with 50 cm^3 of solvent and the amount of sample contained in the ampoule varied between 0.005 and 0.05 g. The calorimeter was calibrated by measuring heat effects of solution of KCl in water [5].

2.3. Densimetry

Solution densities were measured with help bicapillary picnometers (V – 10 cm^3). The picnometers were calibrated with water [6] and aqueous NaCl solutions [7]. All the measurements were carried out at 298.15 K, controlled to 0.005 K. The error in the density measurements was not greater than 2×10^{-5} g cm^{-3}. The solute concentration was varied from 0.01 to 0.25 mol kg^{-1}. All solutions were made up by weight.

3. Results

Results of the calorimetric experiments are summarised in Table 1. The final solute molalities were within the concentration range of 0.0005 to 0.0050 mol kg^{-1}. No concentration dependence was observed in this range. The values of standard enthalpies of solution of infinite dilution obtained in benzene (2.8 kJ mol^{-1}) and acetonitrile (−3.5 kJ mol^{-1}) differ from the data reported in Ref. [8] (−1.88 and −4.8 kJ mol^{-1}, respectively) because those values was determined from a significantly higher concentration range (0.01–0.1 M). Thus, our results are closer to the solution enthalpy at infinite dilution. The value of $\Delta_{\mathrm{soln}}H$ in water is in agreement with that in Ref. [9]. Using the enthalpy of evaporation of 15-crown-5 as

Table 1
The solution and solvation enthalpies of 15-crown-5 in different solvents at infinite dilution at 298.15 K and the enthalpies of 15-crown-5–solvent interactions

Solvent	$\Delta_{\mathrm{soln}}H^0$/ (kJ mol^{-1})	$\Delta_{\mathrm{solv}}H^0$/ (kJ mol^{-1})	$\overline{H}_{\mathrm{int}}$ (kJ mol^{-1})
Carbon tetrachloride	2.82	−76.8	−126.8
Benzene	2.80	−76.8	−131.6
Chloroform	−22.55	−102.4	−158.4
Acetone	1.80	−77.8	−135.2
Pyridine	−3.24	−82.8	−151.6
DMF	−0.94	−80.4	−163.4
DMSO	0.85	−78.8	−175.8
Acetonitrile	−3.24	−83.1	−159.2
Methanol	2.30	−77.3	(−177)
Water	−39.75	−119.3	(−298)
1,4-Dioxane	1.2 [a]	−78.4	−122.5
Tetrahydrofurane	0.7 [a]	−78.9	−133.6

[a] From Ref. [8].

Table 2
Densities and apparent molar volumes of 15-crown-5 in different solvents at 298.15 K

m/(mol kg^{-1})	d/(g cm^{-3})	Φ_v/(cm^3 mol^{-1})	m/(mol kg^{-1})	d/(g cm^{-3})	Φ_v/(cm^3 mol^{-1})
DMF [a]			*Benzene* [d]		
0.00000	0.94394		0.00000	0.87345	
0.02808	0.94493	193.58	0.05942	0.87595	196.50
0.03693	0.94524	193.72	0.07665	0.87673	195.32
0.05524	0.94584	194.26	0.09254	0.87643	195.00
0.08562	0.94681	195.08	0.11900	0.87874	192.70
0.09545	0.94712	195.32	0.15042	0.88029	191.12
0.13307	0.94822	196.35	0.16791	0.88116	190.35
			0.18720	0.88216	189.31
Pyridine [b]			*Ethylacetate* [e]		
0.00000	0.97787		0.000000	0.89458	
0.01879	0.97825	204.03	0.10622	0.89900	193.21
0.03004	0.97849	203.54	0.14521	0.90067	192.50
0.03998	0.97872	202.84	0.18218	0.90226	191.88
0.06356	0.97927	201.93	0.20162	0.90307	191.78
0.07212	0.97952	200.99	0.21609	0.90367	191.72
0.07681	0.97962	201.07			
0.08702	0.97990	200.44			
Carbon tetrachloride [c]			*Acetonitrile* [f]		
0.00000	1.58512		0.00000	0.77682	
0.09172	1.57207	195.77	0.02715	0.77836	188.90
0.13584	1.56772	192.40	0.04315	0.77926	189.11
0.17966	1.56345	189.55	0.04965	0.77963	189.15
0.19072	1.56258	188.68	0.06120	0.78026	189.47
0.22723	1.55984	186.21	0.08502	0.78229	189.84
0.25360	1.55844	183.92	0.09813	0.78158	189.64

[a] $\overline{V}_2^0 = 192.78$, $S_v=26.74$, $\sigma=0.035$, $R=0.9999$.
[b] $\overline{V}_2^0 = 205.00$, $S_v=-51.64$, $\sigma=0.11$, $R=0.9981$.
[c] $\overline{V}_2^0 = 202.33$, $S_v=-71.78$, $\sigma=0.18$, $R=0.9993$.
[d] $\overline{V}_2^0 = 199.84$, $S_v=-56.94$, $\sigma=0.23$, $R=0.9957$.
[e] $\overline{V}_2^0 = 194.60$, $S_v=-13.97$, $\sigma=0.15$, $R=0.9801$.
[f] $\overline{V}_2^0 = 188.54$, $S_v=13.04$, $\sigma=0.035$, $R=0.9960$.

79.57 ± 0.25 kJ mol^{-1} [10], the enthalpy of solvation of crown ether have been evaluated (Table 1).

On the basis of experimental density data, the apparent molar volumes (Φ_v) and limiting partial molar volumes ($\overline{V}_2^0$) of 15-crown-5 were determined in different solvents using the following equations [11].

$$\Phi_v = \frac{M}{d} - \frac{1000(d-d_0)}{m_2 d d_0} \tag{12}$$

$$\Phi_v = \overline{V}_2^0 + S_v m_2 \tag{13}$$

where M is the molar mass of crown ether, d and d_0 the densities of the solution and the solvent, respectively, m_2 the molality of the solution, and S_v the experimental slope. The d and Φ_v data, coefficients of Eq. (13), are presented in Table 2. The correlation coefficients (R) and the standard deviation (σ) are also presented in Table 2.

4. Discussion

The values of the solution and solvation enthalpies of 15-crown-5 vary insignificantly in the series of solvents studied, with the exception of water and chloroform because of the formation of H-bonds with solute molecules. Relative constancy of the $\Delta_{solv}H^0$

Table 3
Molecular parameters and physical properties of solvents at 298.15 K

Solvent	V_1/(cm^3 mol^{-1}) [12]	$\beta\times10^{10}$/ (Pa^{-1}) [12]	$\Delta_{\mathrm{ev}}H$/ (kJ mol^{-1}) [12]	$\rho\times10^3$/ (K^{-1}) [18]	y	$\sigma\times10^8$/ (cm)	$\mu_1\times10^{18}$/ (un.CGSE) [12]	$\alpha_1\times10^{24}$/ (cm^3) [12]	$-\chi_1\times10^{29}$/ (cm^3) [12]
Carbon tetrachloride	97.1	10.910	32.4	1.211	0.5055	5.38	0	10.49	11.09
Benzene	89.9	9.380	33.85	1.202	0.5123	5.27	0	10.32	9.10
Chloroform	80.7		33.17	1.284	0.5014	5.04	1.15	8.48	9.85
1,4-Dioxane	85.7		35.7	1.158	0.5238	5.20	0.45	8.60	8.48
1,2-Dichloroethane	79.4		34.3	1.150	0.5011	5.02	1.86	8.33	9.90
Tetrahydrofuran	81.6		32.0	1.142	0.5112	5.10	1.75	7.93	8.0
Acetone	74.0		30.8	1.470	0.4740	4.81	2.69	6.41	5.37
Ethylacetate	98.5	10.500	35.1	1.432	0.4954	5.37	1.88	8.83	8.98
Pyridine	80.9	6.96 [a]	40.4	1.012	0.5555	5.22	2.37	9.55	8.06
DMF	77.4	6.22	47.5	1.009	0.5753	5.21	3.86	7.90	6.44
DMSO	71.3		52.9	0.982	0.5909	5.11	3.9	7.99	7.34

[a] From Ref. [17].

values is a result of compensation of solute–solvent interactions and cavity formation. A comparison between changes in $\Delta_{\mathrm{solv}}H^0$ and $\Sigma\overline{H}_{\mathrm{int}} = \Delta_{\mathrm{solv}}H^0 - \overline{H}_{\mathrm{cav}}$, where $\overline{H}_{\mathrm{cav}}$ can be estimated from the scaled particle theory [1], demonstrates this tendency.

For 15-crown-5 the solvation ability of the solvents according to enthalpic characteristics (Table 1) decreases in the following order:H_2O>$CHCl_3$>MeCN>Py>DMF>DMSO>MeOH>Me_2CO>C_6H_6=CCl_4. The ability of the solvents towards intermolecular interactions with 15-crown-5, according to enthalpic characteristics (Table 1), decreases in another way: H_2O>1,2-dichloroethane>DMSO>DMF>MeCN>$CHCl_3$>Py>Me_2CO>THF>C_6H_6>CCl_4>1,4-dioxane.

The correlation (Eq. (11)) based on the scaled particle theory allows to establish the pattern of change of $\Delta_{\mathrm{solv}}H^0$ and $\overline{V}_2^0$. The molecular parameters necessary for calculations and physical properties of the solvents are presented in Table 3. We have selected parameters that have been most frequently used in the literature. The results of correlation (Eq. (11)) depend significantly on the selected sizes of molecules. The molecular diameters of the solvents investigated were estimated from enthalpies of evaporation and coefficients of thermal expansion in accordance with

$$\Delta_{\mathrm{evap}}H = RT + \rho RT^2 \frac{(1+2y)^2}{(1-y)^3} \qquad (14)$$

where $y = \pi N\sigma_1^3/6V_1$ is the factor of packing of solvent molecules. The values σ_1, obtained from Eq. (14), are in close agreement with those determined from the gas solubility data [12]. The molecular diameter of 15-crown-5 is found to be $7.43\cdot10^{-8}$ cm, as the diameter of a sphere having volume equivalent to the volume of the molecule, from geometric parameters [13], according to the method described in Ref. [14]. The polarizability of the 15-crown-5 molecule was evaluated from Lorentz–Lorenz relation, at a refractive index n=1.464 [15] and molar volume V_2=198.6 cm^3 mol^{-1} [9], and is found to be 21.7×10^{-24} cm^3 per molecule. The value of diamagnetic susceptibility was estimated to be $21.2\cdot 10^{-29}$ cm^3 per molecule on the basis of the Pascal method [16].

The characteristics at infinite dilution, determined from Eq. (11), are listed in Table 4. The enthalpies of solvation of 15-crown-5 in 1,2-dichloroethane, acetone and DMSO do not submit to any general pattern. The coefficients in Eq. (11) for these solvents differ a little from those in other solvents. It is probably due to differences in packing of solvation spheres and in the state of solute in the solvents indicated. For solutions in water and methanol, the equations of the scaled particle theory cannot be applied.

It is noteworthy that the coefficients A_1 and A_2 of Eq. (11) have different values for solvation enthalpy and limiting partial molar volume. The effective constant of dispersion solute–solvent interactions C_6^{eff} evaluated from $\Delta_{\mathrm{solv}}H^0$ is higher than the theoretical C_6. On the contrary, the C_6^{eff} estimated from $\overline{V}_2^0$ is less than the theoretical C_6. The $(\mu_2^{\mathrm{eff}})^2$ value of the

Table 4
The coefficients of Eq. (11) for correlation of the solvation entalpies and limiting partial molar volumes of 15-crown-5 with solvents properties

Characteristic	Solvents	$A_1 = C_6^{\mathrm{eff}}/C_6$	$(A_2\mu_2^2)\times10^{36}$/ (un.CGSE)^2	R	σ
$\Delta_{\mathrm{solv}}H^0$	carbon tetrachloride, benzene, 1,4-dioxane, chloroform, tetrahydrofuran, pyridine, DMF	1.49	8.27	0.9999	1.52 [a]
$\Delta_{\mathrm{solv}}H^0$	1,2-dichloroethane, acetone, DMSO	1.38	6.95	0.9999	1.7 [a]
$\overline{V}_2^0$	carbon tetrachloride, benzene, ethylacetate, pyridine, DMF	0.92	13.69	0.9998	1.42 [b]

[a] Units: kJ mol^{-1};
[b] Units: cm^3 mol^{-1}.

unperturbed molecule of 15-crown-5 in carbon tetrachloride, benzene, 1,4-dioxane, chloroform, tetrahydrofurane, pyridine and DMF is equal to 8.3 D^2. Thus, the effective dipole moment is 2.9 D, which is close to the experimentally obtained value μ_2 in benzene (3.17 D) [19]. The effective dipole moment of the 15-crown-5 molecule, evaluated from $\overline{V}_2^0$ values (3.7±0.6 D), is greater than those from $\Delta_{\mathrm{solv}}H^0$ values (2.9±0.7 D). The differences observed may be attributed to different sensitivities of $\Delta_{\mathrm{solv}}H^0$ and $\overline{V}_2^0$ values to the effects which do not take into account the assumptions about independence of α_{i}, χ_{i}, σ_{i} and μ_2 parameters on temperature and pressure in Eq. (11).

According to Eq. (11), whose coefficients are listed in Table 4, the estimation of separate contributions of $\Delta_{\mathrm{solv}}H^0$ and $\overline{V}_2^0$ to the total values has been carried out (Appendix AAppendix B). The variation of enthalpic contributions in the series of systems studied are found to be up to 39 kJ mol^{-1} for $\overline{H}_{\mathrm{cav}}$, up to 47 kJ mol^{-1} for $\overline{H}_{\mathrm{dd}}$, and up to 27 kJ mol^{-1} for $\overline{H}_{\mathrm{disp}}$, when the total $\Delta_{\mathrm{solv}}H^0$ varies from −76.2 to −102.4 kJ mol^{-1}. The variations of volume contributions are: 26.5 cm^3 mol^{-1} for $\overline{V}_{\mathrm{cav}}$, 58.4 cm^3 mol^{-1} for $\overline{V}_{\mathrm{dd}}$ and up to 37 cm^3 mol^{-1} for $\overline{V}_{\mathrm{disp}}$, when the total $\overline{V}_2^0$ value varies from 192.8 to 205.0 cm^3 mol^{-1}. Polarization contributions of the solvents and solute to $\Delta_{\mathrm{solv}}H^0$ and $\overline{V}_2^0$ varies insignificantly.

The data obtained testify that the contribution of electrostatic interactions to enthalpic and volume characteristics in the systems studied is considerable. The proportion of partial enthalpy $\overline{H}_{\mathrm{dd}}$ to the total enthalpy of solute–solvent interactions is found to be from zero in nonpolar benzene to 28.5% in dimethylformamide. Medium polarity, according to Eq. (11), is characterized by a complicated parameter

$$\frac{2\mu_1^2}{3kT}\frac{k_2}{V_1\sigma_{12}^3}+\alpha_1\frac{k_3}{V_1\sigma_{12}^3},$$

where k_2 and k_3, depending on the physical parameters of the medium, are specific to the different correlated solution properties (free energy, enthalpy of solvation, partial molar volume, etc.).

Appendix A

Contributions to the solvation enthalpies

The contributions to the solvation enthalpies of 15-crown-5, evaluated according Eq. (11)

Solvent	$\overline{H}_{\mathrm{cav}} - RT(1-\rho T)$/(kJ mol^{-1})	$\overline{H}_{\mathrm{int}}$/(kJ mol^{-1})				$\Delta_{\mathrm{solv}}H^0$/(kJ mol^{-1})	
		dd	ind1	ind2	disp	evaluated	experimental
Carbon tetrachloride	50.0	0.0	−1.7	0.0	−125.2	−76.9	−76.8
Benzene	54.8	0.0	−1.9	0.0	−127.9	−75.0	−76.8
1,4-Dioxane	44.1	−2.7	−1.7	−0.4	−118.5	−79.2	−78.4*
Chloroform	56.0	−4.9	−1.9	−0.3	−150.9	−102.0	−102.4
Tetrahydrofuran	54.7	−10.4	−1.7	−0.6	−122.5	−80.5	−78.9*
Pyridine	68.8	−18.1	−1.9	−0.9	−130.2	−82.3	−82.8
DMF	83.0	−45.7	−1.8	−1.6	−113.6	−79.7	−80.4
1,2-Dichloroethane	59.9	−10.7	−1.6	−0.7	−136.8	−89.9	−90.6*
Acetone	57.4	−23.2	−1.1	−1.2	−110.9	−79.0	−77.8
DMSO	97.0	−42.6	−1.7	−1.3	−130.1	−78.7	−78.8

Appendix B

Contributions to limiting partial molar volumes

The contributions to limiting partial molar volumes of 15-crown-5, evaluated according Eq. (11)

Solvent	$\overline{V}_{\mathrm{cav}} + \beta RT$/(cm^3 mol^{-1})	$\overline{V}_{\mathrm{int}}$/(cm^3 mol^{-1})				$\overline{V}_2^0$/(cm^3 mol^{-1})	
		dd	ind1	ind2	disp	evaluated	experimental
Carbon tetrachloride	287.9	0.0	−3.0	0.0	−84.4	200.5	202.3
Benzene	279.3	0.0	−2.9	0.0	−75.0	201.4	199.8
Ethylacetate	278.55	−15.3	−2.4	−1.5	−65.4	194.0	194.6
Pyridine	293.6	−22.8	−2.4	−2.2	−60.7	205.5	205.0
DMFA	305.9	−58.3	−1.9	−5.7	−47.5	192.5	192.8

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