

Positive and Negative Contributions in the Solvation Enthalpy due to Specific Interactions in Binary Mixtures of C1–C4 *n*-Alkanols and Chloroform with Butan-2-one

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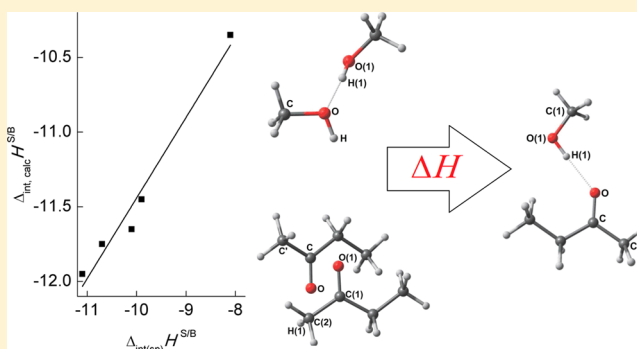
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S Supporting Information

ABSTRACT: In the paper, results of calorimetric measurements, IR spectra, and calculated *ab initio* stabilization energies of dimers are reported for binary systems butan-2-one + (methanol, ethanol, propan-1-ol, butan-1-ol, and chloroform). Changes in the total enthalpy of specific interactions due to dissolution of butan-2-one in the alcohols, calculated using equations derived in previous works, are positive. That results from the endothermic breaking of the O—H...O—H bonds not completely compensated by the exothermic effects of formation of the O—H...O=C ones. Moreover, the concentration of nonbonded molecules of butan-2-one is significant even in dilute solutions, as is evidenced by the shape of the C=O stretching vibrations band in the IR spectra. Apart from that, the spectra do not confirm 1:2 complexes in spite of two lone electron pairs in the carbonyl group of butan-2-one capable of forming the hydrogen bonds. The changes in enthalpy of specific interactions are negative for dilute solutions of alcohols and chloroform in butan-2-one and of butan-2-one in chloroform, because no hydrogen bonds occur in pure butan-2-one. The experimental results are positively correlated with the enthalpies estimated from the *ab initio* energies using a simple “chemical reaction” approach.



1. INTRODUCTION

Two lone electron pairs enable the carbonyl group to accept two protons in hydrogen bonding, while alkanols and chloroform are donors of protons. That causes cross-association of butan-2-one with alkanols and chloroform, and makes their binary mixtures thermodynamically nonideal.^{1–15} Mixing is exothermic with chloroform,¹⁴ and it is endothermic with alkanols: methanol, ethanol, propan-1-ol, and butan-1-ol.^{4,7,15} In the latter process, the formation of O—H...O=C bonds is accompanied by breaking of the O—H...OH ones. Obviously, van der Waals interactions contribute to the total effects of mixing as well. This well-known general picture still requires more explanation. For example, the question of the cross-associate stoichiometry remains open. Undoubtedly, the 1:1 complexes occur in binary mixtures. There are also arguments for C₄H₈O·2 CHCl₃ complexes, based mainly on Raman spectra.¹⁴ However, the band due to the carbonyl group stretching vibrations did not show three distinct peaks that could be unambiguously related to the C=O groups in three different states: free (i.e., non-hydrogen-bonded), single-bonded, and double-bonded. On the contrary, the peaks overlapped significantly and just one absorption maximum was observed.

That made the separation dependent on the function applied to approximate the peaks.¹⁶

Similar proton affinities of butan-2-one, methanol, ethanol, propan-1-ol, and butan-1-ol, equal to 827.3, 754.3, 776.4, 786.5, and 789.2 kJ·mol^{−1}, respectively,¹⁷ make the 1:2 complexes in the mixtures with alcohols rather unfavorable for entropic reasons. Apart from the interactions between unlike molecules, the effects of the solvation sphere formation from the bulk solvent are revealed in changes of thermodynamic functions in the solution.

In previous works,¹⁸ a method of calculation of the specific interactions contribution to the solvation enthalpy was developed. It was successfully tested on more than 300 solute–solvent hydrogen bonded systems, including different proton acceptors and proton donors, systems with weak and strong hydrogen bonds,^{19–21} and self-associated solvents.^{22,23} The method is based on the following approach. In the total enthalpy of solvation, nonspecific and specific contributions

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Table 1. Association Energies^{a,b} of the Dimers of Alcohols, Butan-2-one, and Chloroform and of the 1:1 Complexes of Butan-2-one with Alcohols and Chloroform, Computed for the Geometries Reported in Tables S1–S3 of the Supporting Information

	DFT/B3LYP			MP2 ^c			MP2			B2PLYP		
	ΔE	ΔE_{BSSE}	$\Delta E_{\text{BSSE+ZPE}}$	ΔE	ΔE_{BSSE}	$\Delta E_{\text{BSSE+ZPE}}$	ΔE	ΔE_{BSSE}	$\Delta E_{\text{BSSE+ZPE}}$	ΔE	ΔE_{BSSE}	$\Delta E_{\text{BSSE+ZPE}}$
(CH ₃ OH) ₂	20.6	19.3	14.0	26.1	21.5	16.2	26.8	21.4	16.0	23.2	20.7	15.3
(C ₂ H ₅ OH) ₂	20.8	19.0	14.0	29.2	23.1	18.0	31.1	23.1	17.9	24.5	21.1	16.1
(C ₃ H ₇ OH) ₂	21.1	19.0	14.3	30.6	23.6	18.9	33.1	23.5	18.5	25.3	21.2	16.4
(C ₄ H ₉ OH) ₂	21.2	19.0	14.7	31.3	24.0	19.6	41.7	24.5	19.0	25.6	21.3	16.6
(C ₄ H ₈ O) ₂	13.7	9.8	6.7	34.7	24.1	21.0	43.5	25.8	21.6	23.3	15.6	12.6
(CHCl ₃) ₂	3.2	1.8	1.2	16.1	10.0	9.4	27.4	10.1	8.5	9.0	3.5	2.7
C ₄ H ₈ O·CH ₃ OH	22.2	20.0	15.3	29.8	23.6	18.8	30.3	23.5	18.6	25.6	22.2	17.3
C ₄ H ₈ O·C ₂ H ₅ OH	21.6	19.3	15.0	30.1	23.4	19.2	30.6	23.2	18.7	25.3	21.6	17.2
C ₄ H ₈ O·C ₃ H ₇ OH	21.6	19.3	14.8	30.5	23.5	19.1	31.1	23.3	19.1	25.4	21.6	17.2
C ₄ H ₈ O·C ₄ H ₉ OH	21.5	19.2	15.1	30.6	23.5	19.4	31.1	23.3	19.0	25.4	21.5	17.4
C ₄ H ₈ O·CHCl ₃	18.1	15.7	13.7	30.7	21.3	19.3	38.3	23.1	20.1	23.4	18.4	16.0

^a ΔE in kJ mol^{−1}. ^bBSSE, corrected for the basis set superposition error; ZPE, corrected for the zero-point vibrational energy. ^cResults obtained for single-point calculations from the DFT/B3LYP optimized geometries.

could be distinguished that correspond to changes in energy of molecular interactions of different types that accompany this process. The first contribution is due to van der Waals forces, and the second one reflects the donor–acceptor interactions including hydrogen bonds. On the other hand, the solvation process may be virtually separated into two steps: the formation of a cavity in the neat solvent and filling it with a solute entity, e.g., one molecule. Thus, the enthalpy of solvation is the sum of enthalpies of the cavity formation and of the solute–solvent molecular interactions, both specific as well as nonspecific ones.

In the present work, we report results of calorimetric, IR spectroscopy, and theoretical studies of binary systems butan-2-one + (methanol, ethanol, propan-1-ol, butan-1-ol, and chloroform). Association energies of self- and cross-associates were computed by *ab initio* methods. Partial molar volumes and partial molar isentropic compressions, calculated from the excess functions reported previously,¹ were interpreted in terms of molecular interactions. The solvation enthalpies calculated from the calorimetric data were correlated with those estimated by a quasi-chemical approach from the *ab initio* energies. The stoichiometry of the complexes indispensable in the calculations was deduced from the IR spectra.

2. THEORETICAL CALCULATIONS

Association energies and geometries of the alcohol dimers and of the 1:1 complexes of alcohols and chloroform with butan-2-one were calculated with the Gaussian 09 program package.²⁴ Density functional theory (DFT) with the B3LYP functional^{25,26} and second-order Møller–Plesset perturbation theory (MP2)²⁷ were applied using the Dunning's augmented correlation consistent polarized valence double- ζ (aug-cc-pVDZ) basis set.^{28,29} Calculations by the double hybrid B2PLYP method were also performed.³⁰ The optimum geometries of dimers, 1:1 complexes, and monomers were determined by minimizing the energy with respect to all geometrical parameters of these species. On the basis of the calculated energies for optimized structures, the association energies were appointed with applying the supermolecular approach. In all levels of theory, interaction energies were corrected for the zero-point energies (ZPE) and basis set superposition error (BSSE). BSSE corrections were determined using CP methods.³¹ A similar method of calculations was applied and reported in detail earlier.³² The calculated values of association energies are gathered in Table 1. The B2PLYP

association energies of the alcohol dimers are very close to the negative enthalpies of hydrogen bonding obtained solely from thermodynamic data, equal to 15.1, 16.9, 17.7, and 17.7 kJ·mol^{−1} for methanol, ethanol, propan-1-ol, and butan-1-ol, respectively.¹⁹ The MP2 energies are generally higher than those calculated by DFT/B3LYP and B2PLYP. In the latter, the dispersion energies are neglected or underestimated, which is a general feature of the DFT results.^{33,34} That accounts for the DFT/B3LYP energy being lower by 15 kJ·mol^{−1} than the MP2 one for the butan-2-one dimer. We have also observed such a sequence of the energies, MP2 > B2PLYP > DFT/B3LYP, for other systems.^{32,35–38}

Optimized structures of the studied complexes obtained in the B3LYP/aug-cc-pVDZ calculations are shown in Figure 1. Relevant geometrical parameters computed at this and the two other levels of theory are available as Supporting Information Tables S1–S3. Optimized geometries of respective complexes are similar to each other for all levels of the theory. Notable differences in geometry are evident in the lengths of hydrogen bonds, which well correlate with obtained interaction energies at individual levels of theory.

3. EXPERIMENTAL SECTION

3.1. Chemicals. Chemicals (Aldrich, min. 98%) were distilled and dried according to standard methodologies.³⁹ The purities of 99.9% were reached, as it was estimated from the results of the chromatographic analysis and the Karl Fischer titrations. Details were reported in the previous paper.¹

3.2. Apparatus. The isothermal calorimeter TA Instruments TAM III with a titration input system was used in the measurements of the solution enthalpies at a temperature of 298.15 ± 0.01 K. In each experiment, the solute was injected in consecutive drops of the volume 5–20 μ L into the thermostated glass cell filled with 100 mL of the solvent. An electronically operated 100 μ L syringe fitted with a long gold cannula was used to this end. The cell was equipped with a stirrer, a Joule heater, and a thermistor. The procedure was described in detail earlier.^{23,40} Test measurements of the solution enthalpy of propan-1-ol in water gave the result of −10.16 ± 0.03 kJ·mol^{−1} that agreed well with the recommended value of −10.16 ± 0.02 kJ·mol^{−1} reported by Hallén et al.⁴¹

Calorimetric experiments were carried out for molalities of the solutes in the range from 1.4 to 73.7 mmol·kg^{−1}. In that concentration range, the values of the molar enthalpies of

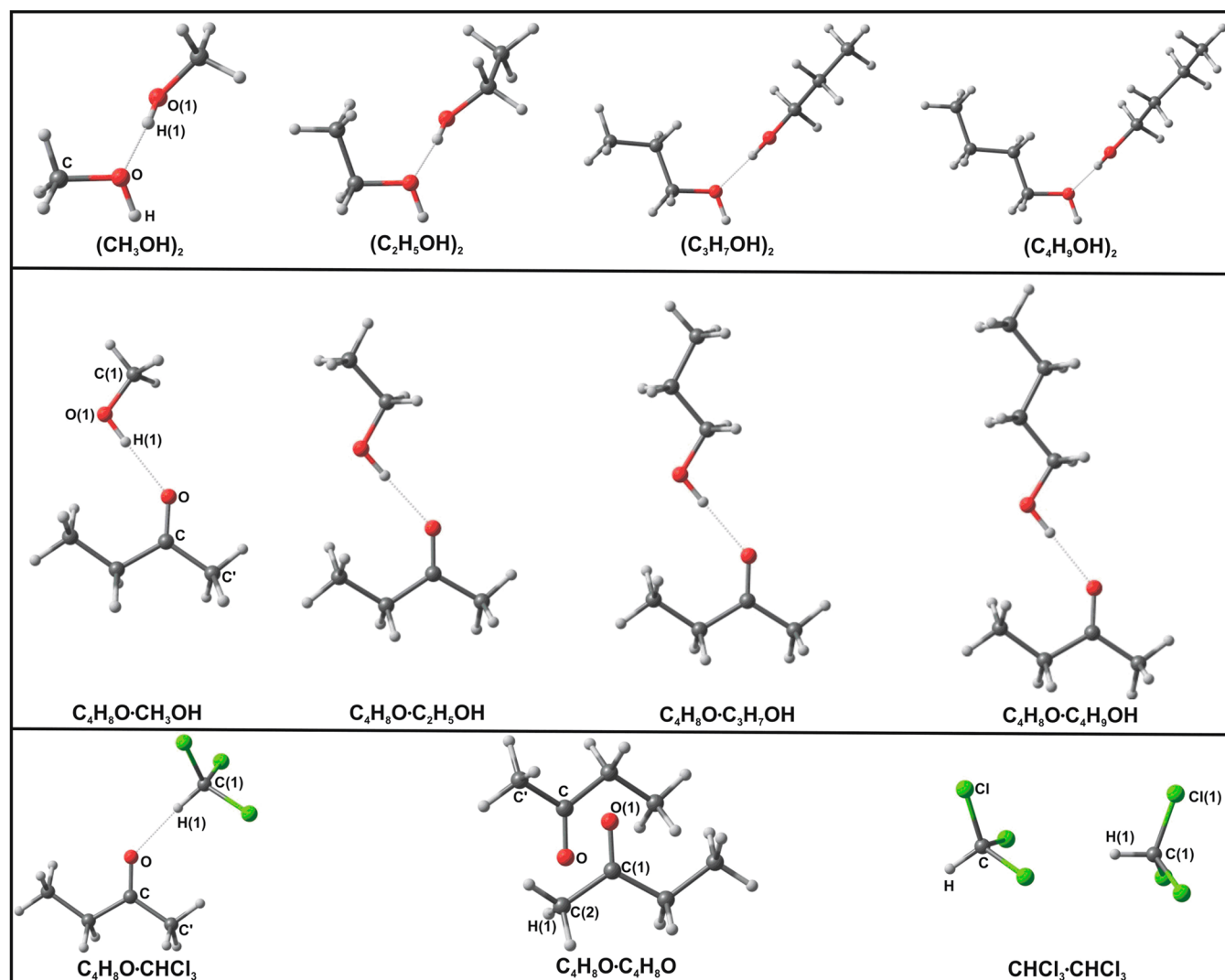


Figure 1. Optimized geometries of the dimers of alcohols, butan-2-one, and chloroform and of the 1:1 complexes of butan-2-one with alcohols and chloroform. Structures obtained from the DFT/B3LYP/aug-cc-pVDZ calculations.

solution proved to be constant for each one of the five systems studied (see Supporting Information Tables S4 and S5). Consequently, the respective mean values might be regarded as the limiting partial molar enthalpies of dilution.

Infrared spectra in the range 4000–400 cm^{-1} were recorded using a FTIR Bruker Vertex 70 spectrometer equipped with a global source, a silicon-based broadband beamsplitter, and a highly sensitive mercury cadmium telluride (MCT) detector. Each measurement consisted of 128 scans that yielded a resolution of 1 cm^{-1} .

4. EXPERIMENTAL RESULTS

4.1. Limiting Partial Enthalpies of Solution and the Enthalpies of Hydrogen Bonding. Limiting partial enthalpies of solution of butan-2-one in four aliphatic alcohols and in chloroform as well as of the alcohols and chloroform in butan-2-one, measured at a temperature of 298.15 K, were reported in Table 2. The dissolutions are endothermic for all butan-2-one–alcohol systems, while they are exothermic for the butan-2-one–chloroform one.

From the experimental results, the enthalpies of solvation of solutes A in solvents S, $\Delta_{\text{solv}}H^{A/S}$, were calculated

$$\Delta_{\text{solv}}H^{A/S} = \Delta_{\text{soln}}H^{A/S} - \Delta_f^gH^A \quad (1)$$

where $\Delta_{\text{soln}}H^{A/S}$ is the experimental limiting partial enthalpy of solution and $\Delta_f^gH^A$ is the vaporization enthalpy. Values of the latter for butan-2-one, the aliphatic alcohols, and chloroform were taken from the literature.⁴² The enthalpy of solvation represents the change of enthalpy that accompanies the isothermal transfer of the solute A from the gas phase to the infinitely dilute solution in solvent S at temperature 298.15 K and pressure 0.1 MPa. The $\Delta_{\text{solv}}H^{A/S}$ values are reported in Table 2.

The following formula derived previously^{23,40} was used to calculate the specific interactions enthalpy

$$\begin{aligned} \Delta_{\text{int(sp)}}H^{A/S} = & \Delta_{\text{soln}}H^{A/S} - \Delta_{\text{soln}}H^{A/C_6H_{12}} \\ & - (\delta_{\text{cav}}h^S - \delta_{\text{cav}}h^{C_6H_{12}})V_{\text{char}}^A \\ & - (a_R + b_R\sqrt{\delta_{\text{cav}}h^S})[\Delta_{\text{soln}}H^{A/S_R} \\ & - \Delta_{\text{soln}}H^{A/C_6H_{12}} - (\delta_{\text{cav}}h^{S_R} - \delta_{\text{cav}}h^{C_6H_{12}})V_{\text{char}}^A] \end{aligned} \quad (2)$$

where $\Delta_{\text{soln}}H^{A/S}$, $\Delta_{\text{soln}}H^{A/S_R}$, and $\Delta_{\text{soln}}H^{A/C_6H_{12}}$ are the solution enthalpies of solute A in the studied solvent S, in standard

Table 2. Limiting Enthalpies of Solution, Enthalpies of Solvation, and Enthalpies of Specific Interactions of Substances (S): Aliphatic Alcohols and Chloroform in Butan-2-one (B) and of Butan-2-one (B) in the Substances (S) at $T = 298.15$ K and $p = 0.1$ MPa

substance	$\Delta_{\text{soln}}H^{S/B}$ (kJ·mol ⁻¹)	$\Delta_{\text{soln}}H^{B/S}$ (kJ·mol ⁻¹)	$\Delta_{\text{int(sp)}}H^{S/B}$ (kJ·mol ⁻¹)	$\Delta_{\text{soln}}H^{B/S}$ (kJ·mol ⁻¹)	$\Delta_{\text{soln}}H^{B/S}$ (kJ·mol ⁻¹)	$\Delta_{\text{int(sp)}}H^{B/S}$ (kJ·mol ⁻¹)
methanol	4.01 ± 0.03	-34.0	-11.1	2.45 ± 0.06	-32.3	2.6
ethanol	6.07 ± 0.02	-36.3	-10.1	3.64 ± 0.04	-31.2	3.1
propan-1-ol	6.02 ± 0.03	-41.5	-9.9	5.50 ± 0.03	-29.3	4.1
butan-1-ol	6.27 ± 0.02	-45.4	-10.7	6.05 ± 0.01	-28.7	4.7
chloroform	-6.79 ± 0.03	-37.9	-8.1	-8.17 ± 0.03	-43.0	-8.5

solvent S_R , and in cyclohexane, respectively; $\delta_{\text{cav}}h^S$, $\delta_{\text{cav}}h^{S_R}$, and $\delta_{\text{cav}}h^{C_6H_{12}}$ are the specific relative cavity formation enthalpies for each solvent; and V_{char}^A is a characteristic volume of solute A.⁴³ The value of $\delta_{\text{cav}}h^S$ represents the enthalpy change during the transfer of an alkane from imaginary solvent S_0 , where the solution enthalpy of the alkane is zero ($\Delta_{\text{soln}}H^{C_nH_{2n+2}/S} = 0$), to the studied solvent S, divided by the characteristic volume $V_{\text{char}}^{C_nH_{2n+2}}$ of the alkane:

$$\delta_{\text{cav}}h^S = \frac{\Delta_{\text{soln}}H^{C_nH_{2n+2}/S}}{V_{\text{char}}^{C_nH_{2n+2}}} \quad (3)$$

For the determination of the specific interactions enthalpy, two standard solvents S_R were used: benzene for the proton acceptor solutes ($a_R = 0.20$, $b_R = 0.38$) and carbon tetrachloride for the proton donor ones ($a_R = 0.34$, $b_R = 0.61$). Data necessary for the calculations of $\Delta_{\text{int(sp)}}H^{A/S}$ via eq 2 can be found in Supporting Information Table S6. The above formulas are valid provided the molecular state of the solvent is the same in the gas phase as in the solution. In this study, we assumed that solutes are monomeric in both states.

The enthalpies of specific interactions calculated from eq 2 are reported in Table 2. These values should not be confused with the energy of the solute–solvent hydrogen bonds, because they result from both the formation and breaking of the hydrogen bonds due to the solvation. The values of $\Delta_{\text{int(sp)}}H^{B/S}$ and $\Delta_{\text{int(sp)}}H^{S/B}$ in butan-2-one–chloroform mixtures are close to one another. A similar result was obtained for the acetone–chloroform system.²⁰

4.2. IR Spectroscopy. Two liquid systems, butan-2-one + chloroform and butan-2-one + propan-1-ol, were studied by FTIR spectroscopy at room temperature. Ten spectra were recorded for each system, for the concentration range from pure butan-2-one to the solute mole fraction 0.9. Pure butan-2-one showed an absorption peak at a wavenumber of 1717 cm^{-1} , that is a well-known effect of stretching vibrations of the carbonyl group.⁴⁴ The peak proved to be almost perfectly well approximated by the equation of Zelsmann and Marechal^{45,46}

$$A = \frac{A^*}{2\mu \cosh[\pi(\tilde{\nu} - \tilde{\nu}_0)/(2\mu)]} \quad (4)$$

where A is the absorption and $\tilde{\nu}$ is the wavenumber, while $\tilde{\nu}_0$, μ , and A^* are the fitting coefficients. A^* is the integral intensity of the band. Approximations with Gaussian and Lorentzian functions gave worse results, as is illustrated in Figure 2.

An addition of chloroform or propan-1-ol to butan-2-one causes a new absorption peak to arise at $\tilde{\nu}_0 \approx 1708\text{ cm}^{-1}$, as a consequence of the formation of hydrogen bonds involving the carbonyl group. Such a shift of absorption peak is typical of ketones in alcoholic solutions.⁴⁴ Linear combination of the two peaks (eq 4) proved to be sufficient to approximate the empirical bands for all the mixtures studied. The results of the

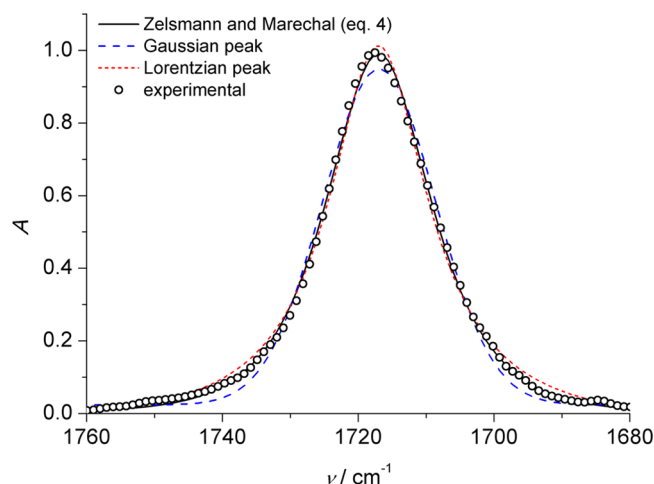


Figure 2. IR stretching vibration band of the carbonyl group in pure butan-2-one.

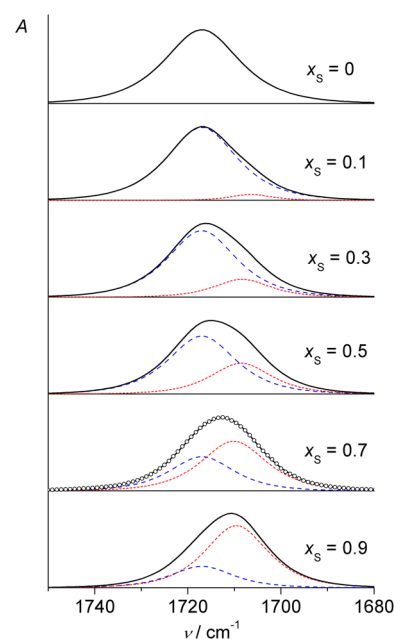


Figure 3. IR spectra of butan-2-one + chloroform in the range of wavenumbers encompassing the band due to stretching vibrations of the carbonyl group. Long dash lines, vibrations of “free” C=O groups; short dash lines, vibrations of hydrogen-bonded carbonyl groups: C=O...H—CCl₃; solid lines, sum of the two component bands. x_S denotes the mole fraction of chloroform in the system. To illustrate the quality of the fit, experimental points were plotted for $x_S = 0.7$.

least-squares fitting are plotted in Figures 3 and 4. Within the measurement error, the empirical and fitted bands are identical. As could be expected, the peak at 1717 cm^{-1} gradually

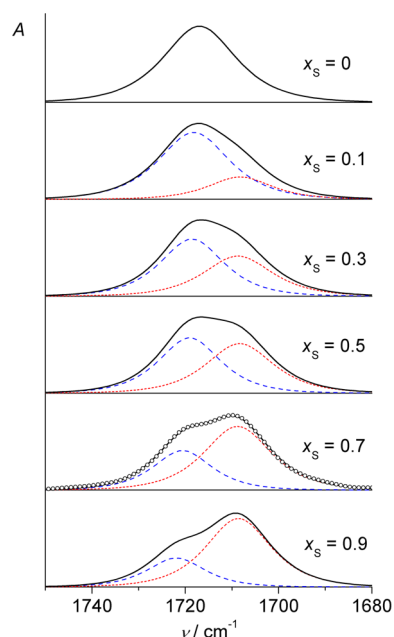


Figure 4. IR spectra of butan-2-one + propan-1-ol in the range of wavenumbers encompassing the band due to stretching vibrations of the carbonyl group. Long dash lines, vibrations of “free” C=O groups; short dash lines, vibrations of hydrogen-bonded carbonyl groups: C=O⋯H—O; solid lines, sum of the two component bands. x_s denotes the mole fraction of propan-1-ol in the system. To illustrate the quality of the fit, experimental points were plotted for $x_s = 0.7$.

decreases with increasing concentration of the hydrogen-bonded butan-2-one. The latter may be roughly estimated from the ratio of the C=O⋯H peak integral intensity to the total integral intensity of the composed band, reported in Table 3 and plotted in Figure 5. It is evident that nonbonded carbonyl groups occur even in dilute solutions of butanone in propan-1-ol and probably also in chloroform. Similar effects were also observed for acetone–methanol and acetone–octan-1-ol mixtures.^{23,47,48}

5. PARTIAL MOLAR VOLUMES AND COMPRESSIONS

Excesses of the partial molar volume and of the partial isentropic compression at a temperature of 298.15 K were calculated from the data reported by us earlier¹ in a way described in detail in a previous paper.³⁷ To this end, two approaches were applied. The first approach is based on the measured raw values of thermodynamic functions, and the second one applies the interpolating polynomials for the concentration dependencies of the excesses reported previously.¹ Good agreement of the results obtained by the two methods of calculation is illustrated in Figures 6 and 7, while the values of the limiting partial functions and their excesses are reported in Table 4.

6. DISCUSSION

The solvation enthalpies are negative for all the systems studied (Table 2). However, trends for the two groups of the systems, butan-2-one in different solvents (group 1) and the solutes in butan-2-one as the solvent (group 2), significantly differ from one another. For the first group, the negative enthalpies of solvation of aliphatic alcohols linearly increase with the increasing length of the alkyl chain. The enthalpy of solvation of chloroform in butan-2-one is in the range of those for the aliphatic alcohols. For the second group, the negative solvation

Table 3. Wavenumbers of Two Absorption Peaks due to Stretching Vibrations of the Carbonyl Group in Butan-2-one and Contributions of the C=O⋯H Peak in the Total Integral Intensity of the Band^a

x_s	$\tilde{\nu}_{\text{C=O}}$ (cm ⁻¹)	$\tilde{\nu}_{\text{C=O}\cdots\text{H}}$ (cm ⁻¹)	contribution (%)
Chloroform			
0	1717		0
0.103	1717	1706	5
0.195	1717	1708	5
0.293	1717	1708	18
0.404	1717	1709	27
0.494	1717	1709	32
0.596	1717	1710	50
0.701	1717	1710	60
0.792	1717	1710	72
0.891	1717	1710	75
Propan-1-ol			
0	1717		0
0.106	1718	1708	23
0.197	1718	1708	33
0.303	1719	1709	43
0.403	1719	1708	45
0.491	1719	1708	49
0.589	1719	1708	49
0.700	1721	1709	65
0.795	1721	1709	66
0.895	1722	1709	73

^a x_s , mole fraction of chloroform or propan-1-ol.

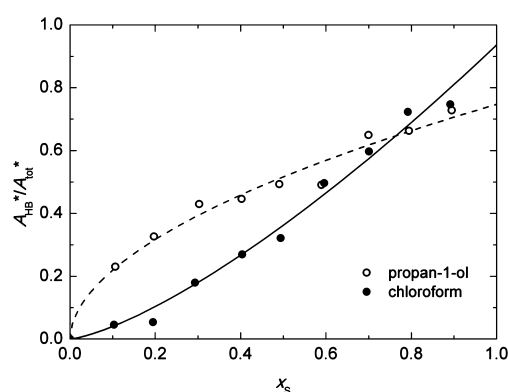


Figure 5. Ratios of the IR peak integral intensities in the band due to stretching vibrations of the carbonyl group in the mixtures of propan-1-ol or chloroform with butanone. A_{HB}^* , intensity of the peak due to the vibrations of hydrogen-bonded C=O groups; A_{tot}^* , total intensity due to the vibrations of hydrogen-bonded and nonbonded C=O groups; x_s , mole fraction of propan-1-ol or chloroform. Points, experimental results; lines, fitted formula $A_{\text{HB}}^*/A_{\text{tot}}^* = ax_s^b$, where a and b are the regression coefficients.

enthalpies of butan-2-one slightly decrease on the elongation of the chain. The negative solvation enthalpy of butan-2-one in chloroform is significantly higher than those of alcohols.

Although resulting from the changes in energy of molecular interactions, the enthalpies of solvation are rather difficult to estimate from the energies computed by the quantum chemical methods. However, the changes in energy of specific interactions caused by the introduction of the solute to an infinitely large amount of the solvent, leading to the $\Delta_{\text{int(sp)}}H^{B/S}$ and $\Delta_{\text{int(sp)}}H^{S/B}$ values reported in Table 2, are closely related to the interaction energies presented in Table 1. A simple quasi-chemical

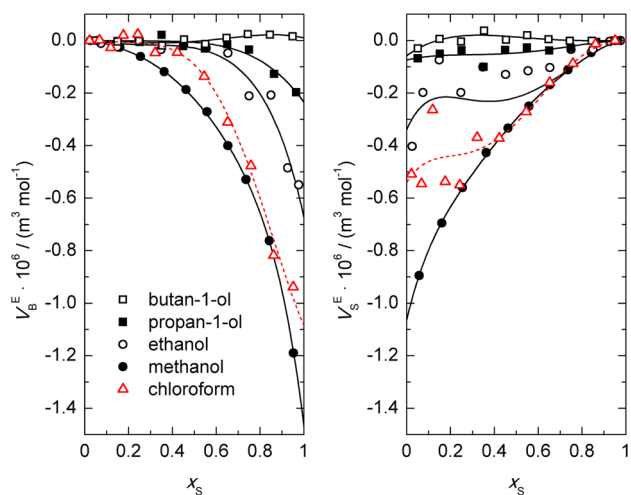


Figure 6. Excess partial molar volumes of butan-2-one (left) and cosolvents (right) in binary mixtures at $T = 298.15$ K. Points were calculated from the raw molar volumes, and lines, from the molar excess functions reported earlier.¹

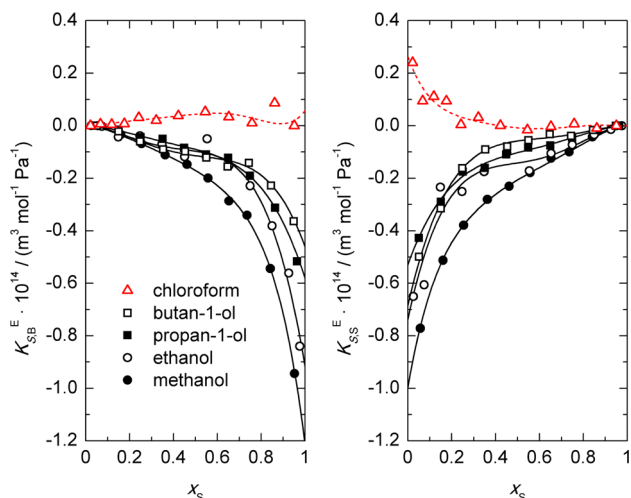
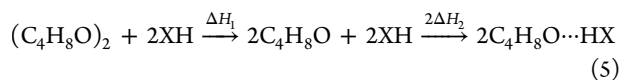
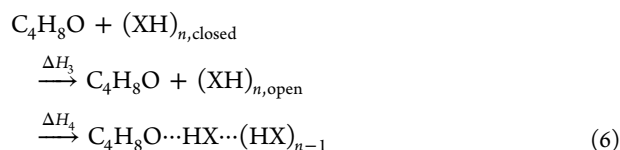


Figure 7. Excess partial molar isentropic compressions of butan-2-one (left) and cosolvents (right) in binary mixtures at $T = 298.15$ K. Points were calculated from the raw molar isentropic compressions, lines, from the molar excess functions reported earlier.¹

approach gives theoretical energies of the interactions consistent with the enthalpies. The following chemical reactions may be suggested for the introduction of the nonbonded solute molecule into the solvent:



for the dissolution of the solutes in butan-2-one and



for the dissolution of butan-2-one in the solvents: methanol, ethanol, propan-1-ol, butan-1-ol, and chloroform. The symbol X stands for $\text{C}_n\text{H}_{2n+1}\text{O}$ or CCl_3 . ΔH_i in eqs 5 and 6 denote the enthalpies of the following processes: dissociation of the

Table 4. Limiting Partial Molar Volumes and Compressions and Their Excess Values in Binary Mixtures of Butan-2-one (B) with Methanol, Ethanol, Propan-1-ol, Butan-1-ol, and Chloroform (S)^a

substance	$V_B^\infty \cdot 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$V_B^{\infty E} \cdot 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$V_S^{\infty} \cdot 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$V_S^{\infty E} \cdot 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	$K_{SB}^\infty \cdot 10^{14}$ ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$)	$K_{SB}^{\infty E} \cdot 10^{14}$ ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$)	$K_{SS}^\infty \cdot 10^{14}$ ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$)	$K_{SS}^{\infty E} \cdot 10^{14}$ ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$)
methanol	88.69	-1.47	39.67	-1.06	6.82	-1.22	3.31	-1.00
ethanol	89.49	-0.67	58.34	-0.34	7.19	-0.92	5.10	-0.74
propan-1-ol	89.94	-0.24	75.08	-0.08	7.57	-0.58	6.14	-0.53
butan-1-ol	90.18	0.01	91.93	-0.06	7.77	-0.46	7.07	-0.68
chloroform	89.05	-1.09	80.22	-0.54	8.10	0.06	6.00	0.26

^aEstimated uncertainties: ca. $0.1 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ for the volume and ca. $0.1 \times 10^{-14} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$ for the isentropic compression.

Table 5. Limiting Enthalpies of Solution and Enthalpies of Molecular Interactions for Substances (S): Aliphatic Alcohols and Chloroform in Butan-2-one (B) and of Butan-2-one in the Substances Calculated from the Interaction Energies Computed at the MP2/aug-cc-pVDZ, B3LYP/aug-cc-pVDZ, and B2PLYP/aug-cc-pVDZ Levels of Theory^a

	$\Delta_{\text{soln,calc}}H^{S/B}$ (kJ mol ⁻¹)			$\Delta_{\text{int,calc}}H^{S/B}$ (kJ mol ⁻¹)			$\Delta_{\text{int,calc}}H^{B/S}$ (kJ mol ⁻¹)		
	MP2	DFT/B3LYP	B2PLYP	MP2	DFT/B3LYP	B2PLYP	MP2	DFT/B3LYP	B2PLYP
methanol	8.2	2.0	4.3	-7.8	-12.0	-11.0	-2.6	-1.3	-2.0
ethanol	10.0	2.4	5.2	-7.9	-11.7	-10.9	-0.8	-1.0	-1.1
propan-1-ol	10.2	2.8	5.5	-8.3	-11.5	-10.9	-0.6	-0.5	-0.8
butan-1-ol	10.8	3.0	5.5	-8.2	-11.8	-11.1	0.0	-0.4	-0.8
chloroform	-0.8	-9.2	-7.0	-9.3	-10.4	-9.7	-11.6	-12.5	-13.3

^aIn this approach, $\Delta_{\text{soln,calc}}H^{S/B} = \Delta_{\text{soln,calc}}H^{B/S}$.

butan-2-one dimer ($i = 1$), formation of the 1:1 complex ($i = 2$), a release of the proton-donating functional group, that consists of breaking of the hydrogen-bonded chains of the solvent molecules ($i = 3$), and formation of the complex of butan-2-one with the associated species of the proton donor solvent ($i = 4$).

It should be noted that van der Waals attractions rather than hydrogen bonds occur between molecules in neat butan-2-one and chloroform. However, the stabilization energies of dimers (Table 1) are too high to be neglected in the considerations. Moreover, the hydrocarbon chains in the butan-2-one dimer enclose the C=O groups (Figure 1), which makes the latter hard to access for the proton-donating functional groups of alcohol or chloroform.

All of the ΔH_i values in eqs 5 and 6 could be estimated from the energies reported in Table 1. For $i = 1, 2$, and 4, the calculations are straightforward

$$\Delta H_1 = \Delta E[(C_4H_8O)_2] \quad (7)$$

$$\Delta H_2 = \Delta H_4 = -\Delta E[C_4H_8O \cdots HX] \quad (8)$$

provided that the cooperativity of hydrogen bonds is neglected in the estimation of ΔH_4 . Although not fully justified, that seems to be reasonable taking into account the approximate nature of the calculations.

Assuming that the $(XH)_n$ chains of alcohols may be of different length and may even form closed loops,⁴⁹ the enthalpies ΔH_3 can be estimated in the following way. Only a terminal XH group of the chain (e.g., OH in alcohols) may form hydrogen bonds with the carbonyl group of the butan-2-one molecule. An increase of the number of terminal groups by 1 mol requires the energy of $\Delta E[(XH)_2]$ to be absorbed by the pure solvent, which is necessary for breaking of the hydrogen bonds in the chains. For linear chains, each consisting of n molecules, that would lead to $k = (n - 1)/n$ mol of “new” terminal groups per 1 mol of the solvent. $k = 0.5$ for dimers ($n = 2$), while $k = \lim_{n \rightarrow \infty} ((n - 1)/n) = 1$ for the chains of infinite length, that are formally equivalent to cyclic aggregates without side branches, and $0.5 < k < 1$ for other values of n . Thus, the enthalpy of the release (cf. eq 6) per 1 mol of the solvent is equal to

$$\Delta H_3 = k\Delta E[(XH)_2] \quad (9)$$

and its maximum value may reach $\Delta E[(XH)_2]$ for breaking of the cyclic aggregates.

Finally, the total changes of enthalpies in eqs 5 and 6 are given by

$$\begin{aligned} \Delta_{\text{int,calc}}H^{S/B} &= \frac{\Delta H_1 + 2\Delta H_2}{2} \\ &= \frac{\Delta E[(C_4H_8O)_2] - 2\Delta E[C_4H_8O \cdots HX]}{2} \end{aligned} \quad (10)$$

and

$$\begin{aligned} \Delta_{\text{int,calc}}H^{B/S} &= \Delta H_3 + \Delta H_4 \\ &= k\Delta E[(XH)_2] - \Delta E[C_4H_8O \cdots HX] \end{aligned} \quad (11)$$

Their values, calculated for $k = 1$, are reported in Table 5. The results remain in good agreement with the enthalpies of the specific interactions, $\Delta_{\text{int(sp)}}H^{B/S}$ and $\Delta_{\text{int(sp)}}H^{S/B}$, estimated in the purely thermodynamic way (Table 2). That is in spite of the van der Waals contribution in the interaction energy calculated theoretically. The correlations between empirical and theoretical enthalpies are particularly good for the changes estimated from the energies computed at the DFT/B3LYP level of theory, as is illustrated in Figure 8. The MP2 energies give the

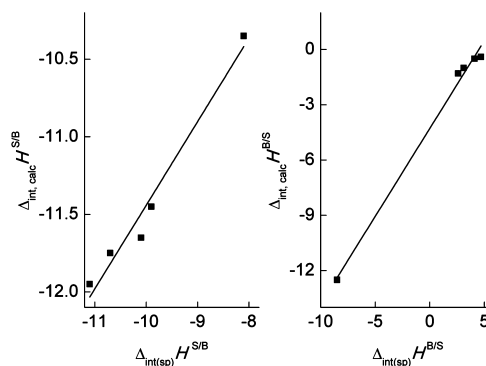


Figure 8. Correlations between the empirical enthalpies of specific interactions and the values estimated from the quantum chemical energies computed at the DFT/B3LYP level of theory for the systems (methanol, ethanol, propan-1-ol, butan-1-ol, or chloroform) + butan-2-one. Points, data reported in Tables 2 and 5; lines, least-squares regressions.

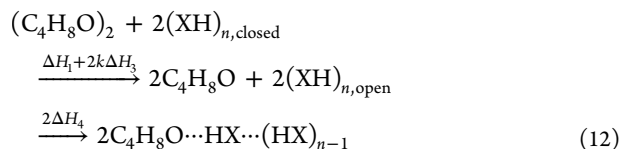
estimated enthalpies slightly different than those of DFT/B3LYP and B2PLYP probably because of higher contributions due to the van der Waals interactions in the former.

Thus, the formation of the $XH \cdots OC_4H_8$ bonds that accompany solvation of the alcohols and chloroform in butan-2-one causes a decrease of the system enthalpy: $\Delta_{\text{int(sp)}}H^{S/B} < 0$. Since the $C_nH_{2n+1}OH \cdots OC_4H_8$ bonds are stronger than the $CCl_3H \cdots OC_4H_8$ ones (cf. DFT/B3LYP and B2PLYP energies in Table 1), the decrease is bigger for the alcoholic systems. For the same reason, the specific interaction enthalpy for butan-2-one in chloroform, $\Delta_{\text{int(sp)}}H^{B/CHCl_3}$, is negative. However, the $O-H \cdots O$ interactions are of similar energy in the dimers of the alcohols and in the butan-2-one–alcohol cross-associates (Table 1). Consequently, if the formation of the cross-associates requires breaking of the alcohol–alcohol bonds, as in the dissolution of

butan-2-one in the alcohols (eq 6), the $\Delta_{\text{int(sp)}}H^{\text{B/S}}$ may be positive, as results from the purely thermodynamic approach (Table 2), or slightly negative, as may be inferred from the estimation based on the quantum chemical energies (Table 5).

1:2 complexes have not been considered in the above discussion in spite of the ability of the butan-2-one molecule to form two hydrogen bonds as an acceptor of protons. There are arguments for both $\text{C}_4\text{H}_8\text{O} \cdot \text{CHCl}_3$ and $\text{C}_4\text{H}_8\text{O} \cdot 2 \text{CHCl}_3$ complexes, based on the IR and Raman spectra, thermodynamics, and quantum chemical calculations.¹⁴ The stabilization energies of $\text{C}_4\text{H}_8\text{O} \cdot 2\text{CHCl}_3$ complexes were by ca. 50% higher than those of $\text{C}_4\text{H}_8\text{O} \cdot \text{CHCl}_3$.¹⁴ Our results of IR measurements, however, do not confirm the 1:2 complexes. Just two absorption peaks rather than three occur in the range of wavenumbers encompassing the band due to stretching vibrations of the butan-2-one carbonyl group, that is illustrated in Figures 3 and 4. With increasing concentration of chloroform, the fraction of H-bonded C=O groups, estimated from the ratio of the peak integral intensities, increases up to 0.94 for infinitely dilute butan-2-one (Figure 5). The incomplete cross-association suggests that the values of ΔH_2 and ΔH_4 (cf. eqs 5 and 6) are less negative than the result of calculations according to eq 8. The effect would be even bigger for the system with propan-1-ol, where the extrapolated fraction of H-bonded C=O groups is only 0.75 (Figure 5). Consequently, the negative contribution to the theoretical enthalpies of molecular interactions (eqs 10 and 11) would be smaller than $\Delta E[\text{C}_4\text{H}_8\text{O} \cdots \text{HX}]$ and the agreement between theoretical and empirical estimations of the solvation enthalpies could be even better.

The chemical reaction approach may be applied to the limiting partial enthalpies of solution. On the dilution, self-associates disappear and cross-associates are formed in the following reaction



where ΔH_1 may be estimated using eqs 7–9, and

$$\Delta_{\text{soln,calc}}H^{\text{S/B}} = \Delta_{\text{soln,calc}}H^{\text{B/S}} = \frac{\Delta H_1 + 2k\Delta H_3 + 2\Delta H_4}{2} \quad (13)$$

The calculation results for $k = 1$ are reported in Table 5.

Although it may seem surprising taking into account the complex molecular mechanism of the solution, the limiting partial enthalpies of solution estimated from the B2PLYP energies of pairwise interactions agree semiquantitatively with the experimental data. The agreement for the DFT/B3LYP is slightly worse, and it is rather poor for the MP2 energies. Since the formation of a cavity for the solute molecule in bulk solvent was not considered in this approach, the estimated enthalpies were independent of which one of the mixture components was the solute and which one was the solvent.

In the previous paper,¹ we explained the excess volumes of the systems (methanol, ethanol, propan-1-ol, butan-1-ol) + butan-2-one by differences in size of the molecules of the alcohols and butan-2-one. That idea is indirectly supported by the lack of convincing correlations between the limiting excess partial volumes (cf. Figure 6 and $V_{\text{B}}^{\text{Eoo}}$ and $V_{\text{S}}^{\text{Eoo}}$ values in Table 4) and the energies of intermolecular interactions (Table 1), and

by the smallest absolute values of $V_{\text{B}}^{\text{Eoo}}$ and $V_{\text{S}}^{\text{Eoo}}$ for the systems with propan-1-ol and especially butan-1-ol. The molecules of the latter are of similar size as those of butan-2-one. Thus, the larger the difference in size of the molecules, the larger are the negative excesses of the partial volumes. Although the excess partial volumes in the system chloroform + butanone are almost as big as those in the mixtures with methanol (Figure 6), the explanation is different. Chloroform does not self-associate through hydrogen bonds, and the stabilization energies of its dimers are much smaller than those of its complexes with butanone. That causes contraction of the volume upon mixing and, consequently, negative excesses of the partial volumes. Another consequence of the formation of the $\text{CCl}_3\text{H} \cdots \text{OC}_4\text{H}_8$ bonds is the negative excess enthalpy of mixing, with the maximum of $-1.4 \text{ kJ} \cdot \text{mol}^{-1}$ for $T = 303 \text{ K}$.¹⁴ The positive excess enthalpies for the mixtures with the alcohols (maximum values of 0.7, 1.1, 1.3, and $1.4 \text{ kJ} \cdot \text{mol}^{-1}$ for methanol, ethanol,^{4,50} propan-1-ol,^{4,15} and butan-1-ol,⁶ respectively) evidence that the exothermic process of formation of the butanone–alcohol hydrogen bonds cannot compensate for the endothermic breaking of the alcohol self-associates. Indeed, the differences between the association energies of the hydrogen-bonded cross- and self-associates are rather small (Table 1), and mixing is an entropy-driven process. That is indirectly corroborated by the IR spectra of butanone + propan-1-ol. Non-hydrogen-bonded molecules of butanone occur even in dilute solutions in the alcohol (Figures 4 and 5).

The limiting excess partial molar compressions of methanol, ethanol, propan-1-ol, butan-1-ol, and chloroform in butan-2-one (Table 4) are positively correlated with the enthalpies of specific interactions $\Delta_{\text{int(sp)}}H^{\text{S/B}}$ reported in Table 2. Thus, the enhanced structuredness of the liquid due to the solute–solvent hydrogen bonds lowers the partial compression of the solute. The limiting excess partial molar compressions of butan-2-one in the alcohols follow the same rule (cf. the values of $K_{\text{S,B}}^{\text{ooE}}$ in Table 4 and $\Delta_{\text{int(sp)}}H^{\text{B/S}}$ in Table 2), most probably because of the similarity of the alcohols as solvents, while that in chloroform clearly stands apart.

7. CONCLUSIONS

Methanol, ethanol, propan-1-ol, butan-1-ol, and chloroform form 1:1 hydrogen-bonded complexes with butan-2-one. Some butanone molecules, however, remain not bonded even in dilute solutions of butan-2-one. Since the energy of the alcohol–alcohol hydrogen bonds is close to that of alcohol–butan-2-one, the changes in total enthalpy of specific interactions due to dissolution of butan-2-one in the alcohols are positive. That results from compensation of the exothermic effects of formation of the $\text{OH} \cdots \text{O}=\text{C}$ bonds by the endothermic breaking of the $\text{O}-\text{H} \cdots \text{O}-\text{H}$ ones. Changes of the hydrogen bonding enthalpies on dissolution of the alcohols in butan-2-one are negative, because the latter does not self-associate due to hydrogen bonds. Similar negative changes accompany dissolution of chloroform in butan-2-one and butan-2-one in chloroform, because of the formation of $\text{CCl}_3\text{H} \cdots \text{O}=\text{C}$ bonds.

The formation of the solute–solvent hydrogen bonds accounts for the variation of partial compressions of methanol, ethanol, propan-1-ol, butan-1-ol, and chloroform in butan-2-one. In the volumetric properties of the alcohol–butan-2-one mixtures, mainly differences in size and shape of the molecules are revealed, while the formation of hydrogen-bonded cross-associates leads to similar effects in the chloroform–butan-2-one system.

■ ASSOCIATED CONTENT

■ Supporting Information

Selected structural parameters for optimized geometries of molecular aggregates computed *ab initio*, experimental enthalpies of solution for the studied systems, enthalpies of solution in inert solvents, enthalpies of the cavity formation and characteristic volumes, complete list of authors for ref 24. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.5b03811.

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Notes

The authors declare no competing financial interest.

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