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Solvent effects on infrared spectroscopic and calorimetric characteristics of aliphatic ketones in binary solvent mixtures

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ABSTRACT: Solution enthalpies of *n*-hexane, acetone, butan-2-one and octan-2-one in a series of tetrachloromethane–acetonitrile mixtures and the carbonyl stretching absorption frequencies in the IR spectra of these ketones were determined. It was found that over the whole range of concentrations (varying from neat tetrachloromethane up to neat acetonitrile) the solvation enthalpy of these compounds can be obtained additively from the contributions of the alkyl and carbonyl fragments. The solvent effect on the solvation enthalpy of the carbonyl group was found to be satisfactorily correlated with the corresponding IR frequency shifts of the C=O group. It was also found that the sensitivities of the carbonyl IR frequencies to the solvent composition are different for various ketones. From both IR and calorimetric data, the preferential solvation parameters were evaluated. The differences between the IR spectroscopic and calorimetric data are discussed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: calorimetry; IR spectra; ketones; solvation

INTRODUCTION

Solvent effects on IR band frequencies and intensities are well known, and there are several excellent reviews devoted to these problems (see, e.g., Refs. 1–3). The most extensively studied were the IR bands belonging to characteristic stretching vibrations of solute molecules. There are numerous studies of the solvent influence on C≡O,[2,4,5] S=O,[6] P=O[7] and C=O group frequencies.[8–12] The observed effects are usually subdivided into those due to specific (e.g. hydrogen bond formation) and non-specific (electrostatic and dispersion) interactions.

A specific interaction usually results in the appearance of new bands due to the AH···B complex formed by an H-bond donor (A-H) with an H-bond acceptor (B). The frequency shifts of A-H stretching vibrations due to the H-bond formation have been thoroughly studied[13–16] and will not be considered here. The shifts of $\nu_{P=O}$, $\nu_{S=O}$ and $\nu_{C=O}$ bands of H-bond acceptors are also well known.[6–11] It should be noted that in some cases no new bands appear on H-bond formation, and only the shifts of the existing bands occur. This is usually the case when the H-bonds are relatively weak. Examples of such systems (e.g. Cl_3C—H···O=C—R) have been extensively studied by Nyquist *et al.*[9,12]

The non-specific solvent effects on the IR band frequencies and intensities are usually considered within the framework of the Onsager reaction field model.[2–6,8,11] This model describes the interaction between the dipole of the oscillating group and the surrounding continuous dielectric medium. The solvation shell of the solute is assumed to be spherical (or ellipsoidal) and totally isotropic. Hence no difference is made between the immediate surroundings of dipolar and non-polar fragments of the same solute molecule.

It seemed of interest to correlate the solvent-induced IR frequency shifts of the solute with thermodynamic characteristics of solute–solvent interactions, obtained from calorimetric experiments. A large quantity of data on solution and solvation enthalpies has been documented (see, e.g., Refs 17–19). Analysis of these data enables one to draw conclusions about different types of solute–solvent interactions in the systems under study. Thus, on the basis of the documented thermodynamic data, scales of hydrogen-bond basicity and acidity were designed.[20–22]

It should be kept in mind that the direct comparison of IR and calorimetric data could reveal some apparent contradictions. For example, it is well known that the larger the dipole moment of the group under study, the greater is the solvent effect on the IR frequencies to be expected.[1–3] On the other hand, it has been shown that the differences between solvation enthalpies of *o*- and *p*-dichlorobenzenes (having essentially different dipole moments) in a wide number of solvents (including both polar and non-polar types) are the same to within 2 kJ

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mol^{-1}.[23] Similar results have been obtained for *o*-, *m*- and *p*-isomers of dinitrobenzene,[23] *cis*- and *trans*-isomers of dichloroethylene[24] *cis*- and *trans*-isomers of dicyanoethylene.[23] It has been concluded that the solute's dipole[23,24] and quadrupole[25] moments do not noticeaby affect the enthalpy and free energy of non-specific solvation.[23–29]

There are several reasons for the apparent contradictions between calorimetric and IR spectroscopic data. First, the solvation enthalpy characterizes the interaction of the solvent shell with a solute molecule as a whole. However, only the interactions of the solvent molecules with a certain molecular group of the solute are important when the solvent effect on the IR band is considered.

Second, it is known that the solvation enthalpy contains the contributions of both solute–solvent and solvent–solvent interactions. The contribution of the solvent–solvent interactions is usually subdivided into the 'cavity' and the 'solvent reorganization' terms.[30,31] The meaning of the former term is the enthalpy necessary to form a cavity having the size of a solute molecule. The latter term reflects the weakening of the solvent–solvent interactions as a result of reorientation of solvent molecules in the solvation shell. Such reorganization also makes a certain contribution to the observed thermodynamic parameter of solvation. At the same time, the solute–solvent interactions (but not the solvent–solvent interactions) are mainly responsible for the frequency shifts in infrared spectra.

Third, it should also be noted that various types of intermolecular interactions (electrostatic, dispersion and specific) can reveal themselves differently in IR and thermodynamic data.

Our previous studies were devoted to the analysis of the contributions of various types of intermolecular interactions to the solvation enthalpies and free energies.[23–29,32,33] The aim of the present work was to establish whether the changes in the vibrational frequencies of the solute and the solvation enthalpies are due to the same factors or not. A useful approach to this problem is to study solvation effects in binary solvent mixtures, which allows one to compare thermodynamic and non-thermodynamic data within the concept of local composition of the solvent shell.[34,35] To make a correct correlation of the experimental data it is also necessary to divide the solvation enthalpies of compounds into the contributions of their molecular groups.

EXPERIMENTAL

Tetrachloromethane, acetonitrile and ketones were commercial products with purities of not less than 99%. They were purified and dried according to recommended methods.[36] The residual water content was determined by electrochemical titration in Karl Fischer reagent medium according to the recommendations in Ref. 37. The concentrations were found to be less than 0.05 mol% for ketones and 0.01 mol% for other substances.

Solution enthalpies were measured at 298 K with a differential quasi-adiabatic calorimeter. The technique for the determination of the heat effects was described in more detail earlier.[23,38] The volume of the calorimetric cell was 100 ml. The final solute concentration did not exceed 0.03 mol 1^{-1}. The absence of a concentration dependence of the heat effects was controlled by successive dissolution of four weighed samples. The values of the solution enthalpies given in Table 1 are the average of 4–6 measurements. The standard deviations of solution enthalpies are also given in Table 1.

The carbonyl stretching vibrational frequencies ($\nu_{C=O}$) were registered at 298 K with a Specord M80 IR spectrometer combined with a computer. The ketone concentration in the IR spectroscopic experiments was varied in the range 1.3×10^{-2}–1.7×10^{-2} mol 1^{-1}. It is well known that at this concentration the self-association of ketones can be neglected.[8,39]. This was confirmed by the absence of spectral changes on further dilution of the ketones. The reproducibility of $\nu_{C=O}$ values was better than 0.05 cm^{-1}. The reproducibility of the scale of wavenumbers was systematically controlled by the IR absorptions of a polystyrene film.

Table 1. Solution enthalpies (ΔH_{sol}, kJ/mol) of *n*-hexane and some aliphatic ketones in tetrachloromethane–acetonitrile mixtures of various composition at 298 K. X_2 is the mole fraction of acetonitrile in the mixture

X_2	*n*-Hexane	Acetone	Butan-2-one	Octan-2-one
0.000	1.63 ± 0.08	2.70 ± 0.08	1.76 ± 0.07	1.15 ± 0.02
0.018	1.68 ± 0.06	1.87 ± 0.05	0.89 ± 0.01	0.65 ± 0.02
0.088	2.06 ± 0.06	0.42 ± 0.05	−0.36 ± 0.05	−0.71 ± 0.04
0.169	2.46 ± 0.08	−0.23 ± 0.05	−0.86 ± 0.03	−0.83 ± 0.06
0.259	2.93 ± 0.08	−0.52 ± 0.05	−1.09 ± 0.06	−0.88 ± 0.05
0.379	3.51 ± 0.08	−0.73 ± 0.05	−1.24 ± 0.02	−0.62 ± 0.04
0.550	4.56 ± 0.08	−0.83 ± 0.05	−1.27 ± 0.02	−0.18 ± 0.02
0.691	5.77 ± 0.08	−0.81 ± 0.05	−1.07 ± 0.02	0.64 ± 0.03
0.810	6.92 ± 0.11	−0.73 ± 0.05	−0.77 ± 0.02	1.68 ± 0.04
0.880	7.80 ± 0.12	−0.64 ± 0.05	−0.52 ± 0.02	2.46 ± 0.09
1.000	9.75 ± 0.16	−0.38 ± 0.05	0.08 ± 0.01	4.11 ± 0.13

To obtain the preferential solvation parameter, the Q-values were calculated for each investigated solvent composition (Q_i) using equation (6). Then the dispersions for each point (δQ_i) were evaluated:

$$\delta^2(Q_i) = \left[\frac{1}{t_i(T_i - T_2)^2}\right]^2 \delta^2(T_1) + \left[\frac{T_1 - T_i}{t_i(T_i - T_2)^2}\right]^2 \delta^2(T_2) + \left[\frac{T_1 - T_2}{t_i(T_i - T_2)^2}\right]^2 \delta^2(T_i) \quad (1)$$

where T_1, T_2 and T_i are the values of the property under study measured for the neat components 1 and 2 (tetrachloromethane, acetonitrile) and the mixed solvent, respectively; t_i is the ratio $t_i = X_2/X_1$; X_2 and X_1 are the mole fractions of acetonitrile and tetrachloromethane in the binary mixture. Then the weighted average of Q_i was calculated using the inverse dispersions as the weight coefficients.

RESULTS AND DISCUSSION

It is well known that the position of the carbonyl stretching absorption in the IR spectrum of ketones ($\nu_{C=O}$) is strongly medium dependent.[8,39] There is a solid basis for believing that this dependence is caused by the change in the interaction between the carbonyl group and the solvent molecule. From the standpoint of solvation thermodynamics, aliphatic ketones are of particular interest since they consist of groups the solvation trends of which are different. First, it should be noted that the carbonyl group of ketones is capable of specific interaction with hydrogen-bond donor (HBD) solvents. Second, as has been shown earlier,[26,32] the dispersion interaction energies per unit volume or surface area of a solute molecule are different for carbonyl and alkyl groups.

Various types of the solute–solvent interaction (i.e. specific and non-specific) can affect the carbonyl IR absorption band in different manners. Therefore, in order to simplify the situation, it would be desirable to select a series of solvents unable to undergo specific interactions with the carbonyl group. However, the number of such solvents is very limited. Furthermore, the solution enthalpies of ketones in such solvents differ very slightly from one solvent to another. In this work, binary mixtures of acetonitrile and tetrachloromethane were selected as the solvent series. Although acetonitrile possesses some weak HBD ability,[40,41] the ratio of the energies of specific and non-specific interactions between the C=O group of the ketone and the molecule of acetonitrile is likely to remain the same over the whole concentration range.

When considering solvation in mixed solvents, particular attention has to be focused on the phenomenon of preferential solvation. The simplest approach to its analysis assumes the binary solvent mixture to consist of two immiscible phases, S_1 and S_2.[42] The preferential solvation parameter (Q) of any solute (A_i) is the distribution coefficient between these two phases, according to the equation

$$Q = C^{A}_{S_1}/C^{A}_{S_2} \quad (2)$$

where C^{A}_{S} is the concentration of the solute (A) in a phase of the solvent S.

The deviation of the preferential solvation parameter (Q) from unity characterizes the preferential solvation of the solute by one of the two solvent components. The magnitude of some physico-chemical property T of the solute in the binary mixture can be calculated from the magnitudes T_1 and T_2, measured for the solutions in neat components 1 and 2:

$$T = \frac{T_1 + T_2 Q(X_2/X_1)}{1 + Q(X_2/X_1)} \quad (3)$$

where X_1 and X_2 are the mole fractions of components 1 and 2 in the binary solvent mixture.

The model assuming an equilibrium between solvates of two kinds in the mixed solvent mixture[43] and the model considering the mole fraction of each component of the solvent mixture in the microsphere of solvation[44] lead to similar equations. In the first case,[43] the Q-parameter means the equilibrium constant between two solvates:

$$A(S_1) + S_2 \rightleftharpoons A(S_2) + S_1 \quad (4)$$

In the second case,[44] the preferential solvation parameter is the ratio

$$Q = \frac{x_2^S/x_1^S}{x_2^0/x_1^0} \quad (5)$$

where x^{S}_{1} and x^{0}_{1} are the mole fractions of solvent 1 in the microsphere of solvation and in the bulk of the solvent mixture, respectively.

Equation (3) can be solved for the unknown Q value using the experimental magnitudes of T, T_1 and T_2:

$$Q = \frac{X_1(T - T_1)}{X_2(T_2 - T_1)} \quad (6)$$

However, it should be noted that the preferential solvation parameter can be calculated only if the value T lies between T_1 and T_2. As is evident from Table 1, this condition is not met for the solution enthalpies of aliphatic ketones in mixtures of tetrachloromethane and acetonitrile.

Instead of the solution enthalpies, it is more convenient to use the transfer enthalpies, ΔH^{A}_{trs}, for comparison of the solvent effects for a series of solutes:

$$\Delta H^{A}_{trs} = \Delta H^{A/S}_{soln} - \Delta H^{A/CCl_4}_{soln} \quad (7)$$

where $\Delta H^{A/S}_{soln}$ is the solution enthalpy of solute A in

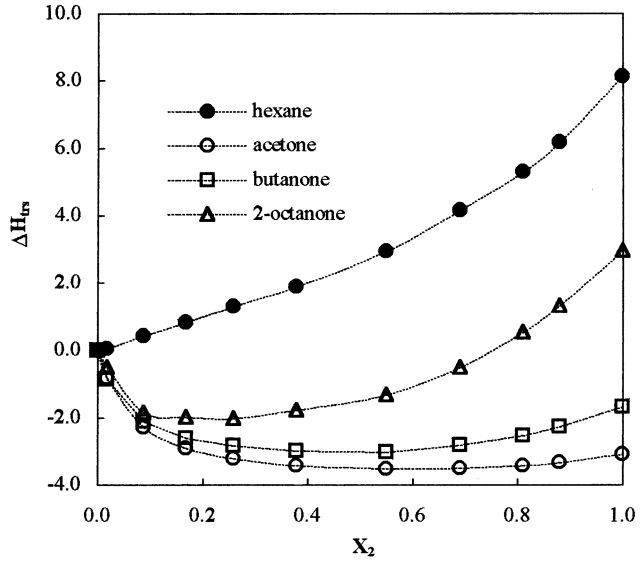

Figure 1. The transfer enthalpies (ΔH_{trs}, kJ/mol) of *n*-hexane and aliphatic ketones as function of the mole fraction of acetonitrile (X_2) in the mixed solvents

solvent S. In this work, the transfer enthalpies were calculated using tetrachloromethane as the reference solvent. The transfer enthalpy does not contain a term for solute–solute interactions or for solvation enthalpy, which is determined as the difference between solution enthalpy ($\Delta H^{A/S}{}_{soln}$) of a solute A in solvent S and the vaporization enthalpy ($\Delta H^{A}{}_{v}$):

$$\Delta H^{A/S}_{solv} = \Delta H^{A/S}_{soln} - \Delta H^{A}_{v} \qquad (8)$$

The transfer enthalpies of acetone, butan-2-one and octan-2-one plotted against the molar fraction of acetonitrile are shown in Fig. 1. As can be seen, there are no linear relationships between the transfer enthalpies and the solvent composition. This indicates the presence of preferential solvation of the solute. However, the character of the solvent composition dependences for ketones differs from that for *n*-hexane. The transfer enthalpy of *n*-hexane is a monotonically increasing function of the concentration of acetonitrile, but the dependences for all the investigated ketones pass through a minimum. This is the reason why previously mentioned models of preferential solvation [equation (3)] are inapplicable for describing the transfer enthalpies of ketones.

Comparing the relationships plotted in Fig. 1, it can be assumed that the alkyl groups of ketones are preferentially solvated by tetrachloromethane whereas the carbonyl group is selectively solvated by acetonitrile.

Since alkyl and carbonyl groups of aliphatic ketones are preferentially solvated by different components of the solvent mixture, it would be of interest to determine the contribution of the carbonyl group to the transfer enthalpy of the ketones. This can be made, assuming the additivity of the solvation enthalpy of ketones, with respect to the group composition of their molecules. In this case,

$$\Delta H^{R_1COR_2}_{trs} = \Delta H^{CO}_{trs} + \Delta H^{R_1,R_2}_{trs} \qquad (9)$$

where H_{trs} is the transfer enthalpy.

It has been shown earlier[33] that the solution enthalpies of liquid saturated hydrocarbons are proportional to their molar refraction (MR). Hence the transfer enthalpies of alkanes should also be proportional to their molar refraction. On this basis, the contribution of alkyl groups to the transfer enthalpy of ketones can be calculated using the transfer enthalpy of *n*-hexane, its molar refraction and the contribution of the alkyl groups to the molar refraction of the ketone:

$$\Delta H^{R_1,R_2}_{trs} = \Delta H^{n\text{-hexane}}_{trs} \frac{MR^{R_1} + MR^{R_2}}{MR^{n\text{-hexane}}} \qquad (10)$$

The molar refractions of *n*-hexane and alkyl groups ($MR^{CH_3} = 5.65$, $MR^{C_2H_5} = 10.30$, $MR^{C_6H_{13}} = 28.91$, $MR^{n\text{-hexane}} = 29.96$) were taken from Ref. 45. Then, the contribution of the carbonyl group can be calculated from equation (9) using the experimentally determined transfer enthalpies of the ketones.

The contributions of the carbonyl group to the transfer enthalpies of acetone, butan-2-one and octan-2-one are plotted against the mole fraction of acetonitrile in Fig. 2. It is obvious that such a correlation for the alkyl group contribution is similar to that for the transfer enthalpy of *n*-hexane. The contribution of the carbonyl group, in

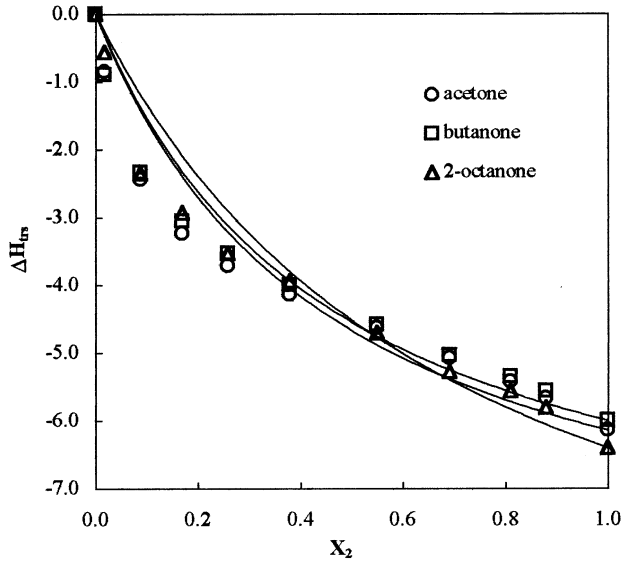

Figure 2. The contributions of the carbonyl groups of aliphatic ketones to their transfer enthalpies ($\Delta H^{CO}{}_{trs}$, kJ/mol) as a function of the mole fraction of acetonitrile (X_2) in the mixed solvents. Continuous curves show the calculated dependence, obtained by fitting the data by Eq. (3) ($Q = 3.54$, 3.64 and 3.14 for acetone, butan-2-one and octan-2-one, respectively)

contrast, decreases monotonically with increasing content of acetonitrile. Because of this, equation (3) may be formally applied to them. The calculated values of the preferential solvation parameter of the carbonyl group were found to be 3.54 ± 0.35, 3.64 ± 0.33 and 3.14 ± 0.60 for acetone, butan-2-one and octan-2-one, respectively.

It is important to note that the *Q*-values of the carbonyl group of all the ketones studied are nearly the same (within the errors of determination) at any composition of the binary solvent mixture. This justifies the applicability of the group additivity principle to the transfer enthalpies of the investigated ketones.

It is widely accepted that the solvent effect on the carbonyl stretching absorption frequency of ketones is mainly due to intermolecular interactions of the carbonyl group with its immediate solvation shell. Hence it is of interest to compare the IR data with the above calculated contribution of the carbonyl group to the transfer enthalpy.

We determined the wavenumbers of the carbonyl stretching absorption ($\nu_{C=O}$) of all ketones at the same compositions of the binary solvent mixture. These data are given in Table 2. The dependences of $\nu_{C=O}$ on the mole fraction of acetonitrile have a complex shape, as can be seen in Fig. 3.

It is of particular interest to correlate the carbonyl wavenumber shifts with the contributions of the C=O group to the transfer enthalpies of ketones. These correlations are shown in Fig. 4. As can be seen, the correlations for all the ketones are nearly linear (the correlation coefficients for acetone, butan-2-one and octan-2-one are 0.993, 0.995 and 0.993, respectively). This means that both $\nu_{C=O}$ and the solvation enthalpy of the carbonyl group are determined mainly by the same factors. However, the slopes of the correlations are different. That is, the sensitivity of $\nu_{C=O}$ to changes in the solvent polarity depends on the alkyl groups of the ketone, in contrast to the solvation enthalpy of the carbonyl group.

Table 2. The carbonyl stretching absorption wavenumbers ($\nu_{C=O}$, cm^{-1}) of some aliphatic ketones in tetrachloromethane–acetonitrile mixtures of various composition at 298 K. X_2 is the mole fraction of acetonitrile in the mixture

X_2	Acetone	Butan-2-one	Octan-2-one
0.000	1718.59 ± 0.05	1720.9 ± 0.05	1719.20 ± 0.05
0.018	1717.17 ± 0.05	1720.2 ± 0.05	1718.53 ± 0.05
0.088	1716.57 ± 0.05	1718.6 ± 0.05	1717.20 ± 0.05
0.169	1715.83 ± 0.05	1717.6 ± 0.05	1716.32 ± 0.05
0.259	1715.37 ± 0.05	1716.7 ± 0.05	1715.46 ± 0.05
0.379	1714.97 ± 0.05	1716.0 ± 0.05	1714.85 ± 0.05
0.550	1714.43 ± 0.05	1715.3 ± 0.05	1714.08 ± 0.05
0.691	1714.12 ± 0.05	1714.8 ± 0.05	1713.55 ± 0.05
0.810	1714.02 ± 0.05	1714.4 ± 0.05	1713.32 ± 0.05
0.880	1713.79 ± 0.05	1714.2 ± 0.05	1713.17 ± 0.05
1.000	1713.81 ± 0.05	1714.0 ± 0.05	1712.79 ± 0.05

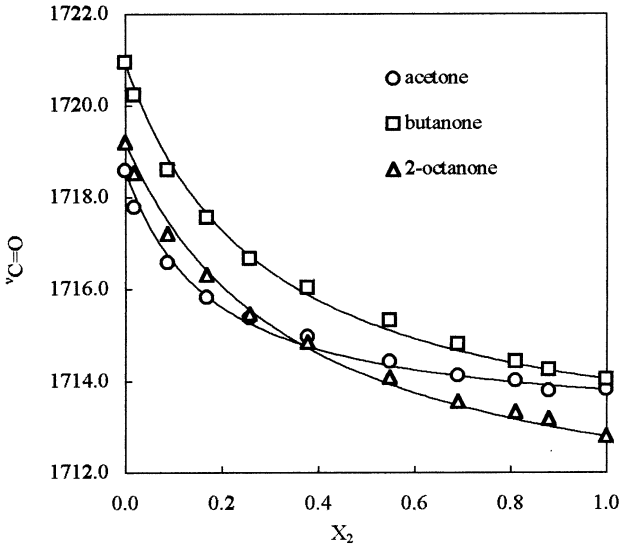

Figure 3. The carbonyl stretching absorption wavenumbers ($\nu_{C=O}$, cm^{-1}) of aliphatic ketones as a function of the mole fraction of acetonitrile (X_2) in the mixed solvents. Continuous curves show the calculated dependence, obtained by fitting the data by Eq. (3) ($Q = 6.60$, 4.54 and 3.85 for acetone, butan-2-one and octan-2-one, respectively)

Solvation enthalpy is often considered as consisting of two terms:[46]

$$\Delta H^{CO}_{trs} = \Delta H^{CO}_{trs(solv--solv\ int.)} + \Delta H^{CO}_{trs(solv--solute\ int.)} \quad (11)$$

As has been mentioned above, the contribution of the solvent–solvent interactions can be represented by the

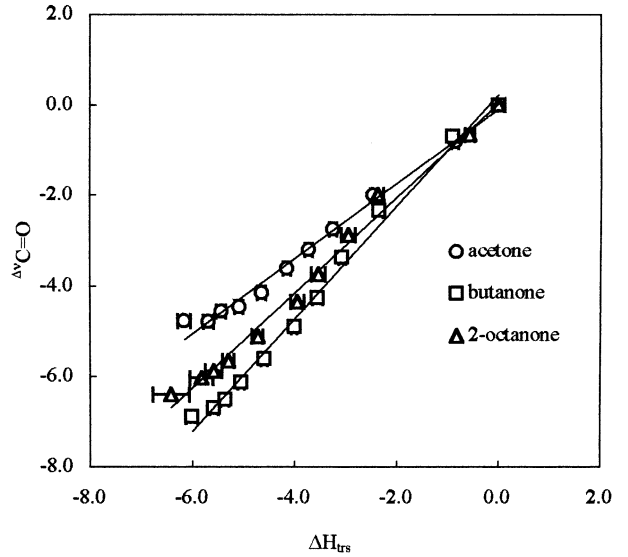

Figure 4. Correlations of the carbonyl stretching absorption wavenumbers (referenced to tetrachloromethane) of aliphatic ketones ($\nu_{C=O}$, cm^{-1}) with the contributions of the carbonyl groups to the transfer enthalpies (ΔH^{CO}_{trs}, kJ/mol). The errors of estimation are also shown

sum of 'cavity' and 'solvent reorganization' terms[30,31]. Thus,

$$\Delta H^{CO}_{trs} = \Delta H^{CO}_{trs(cav)} + \Delta H^{CO}_{trs(reorg)} + \Delta H^{CO}_{trs(solv--solute\ int.)} \quad (12)$$

The three terms on the right-hand side of equation (12) reflect three steps modelling the solvation process:[31]

Step I. Creation in the solvent of an empty cavity having the size of the solute created.

Step II. Introduction of the solute molecule into the cavity created in the solvent. The solute polarizes the solvent molecules, including some reorganization of the solvent molecules around the cavity. The solvent molecules are reoriented so that their mutual interactions are weakened.

Step III. Turning on of the solute–solvent interactions yields the 'charging' energy.

One would expect a better correlation of the carbonyl wavenumber shifts with the interaction enthalpy [$\Delta H^{CO}_{trs\ (solv–solute\ int.)}$] than with the transfer enthalpy of the cabonyl group. The 'cavity' term [$\Delta H^{CO}_{trs\ (cav)}$] can be calculated using the method developed in Ref. 47:

$$\Delta H^{CO}_{trs(cav)} = \Delta H^{n\text{-hexane}}_{trs} \frac{MR^{CO}}{MR^{n\text{-hexane}}} \quad (13)$$

However, there is no adequate method evluating the 'solvent reorganization' term [$\Delta H^{CO}_{trs\ (reorg)}$]. A trivial solution is to neglect this term; this makes no substantial modification to the correlations plotted in Fig. 4, apart from a slight decrease in the correlation coefficients.

Some additional information permits the determination of the preferential solvation parameters calculated from IR spectroscopic data. These values were found to be 6.60 ± 0.42, 4.54 ± 0.20 and 3.85 ± 0.19 for acetone, butan-2-one and octan-2-one, respectively.

One can see from Fig. 3, and to a greater extent from Fig. 2, that there are systematic deviations of the experimental points from the curve calculated by fitting equation (3). These deviations unequivocally show that an improvement of these models is necessary in order to obtain better agreement with the experiment. Nevertheless, we have limited ourselves to the simplest model of preferential solvation.[42] Although the agreement becomes better when using more complex approaches (e.g. as described in Refs. 43, 44 and 48), we thought that, within the framework of this study, such an improvement will lead mainly to an increase of the number of parameters.

The discrepancies between the *Q*-values obtained from the calorimetric and IR spectroscopic data are clear. Enlargement of the alkyl group gives rise to a slight decrease in the IR-determined *Q*-values. It seems likely that this phenomenon is due to shielding of the carbonyl group by the alkyl groups. Actually, a good correlation is observed between the IR-determined *Q* values and the Koppel–Palm steric hindrance constants[49] of alkyl groups ($CH_3 = 0$, $C_2H_5 = 0.27$, $n\text{-}C_6H_{13} = 0.6$).

CONCLUSIONS

The solvation enthalpies of acetone, butan-2-one and octan-2-one in binary solvent mixtures of tetrachloromethane with acetonitrile are each additive with the respect to the group composition of the ketones. Further, the close to linear correlations between the recalculated calorimetric and IR spectroscopic data show the qualitative agreement in the interpretation of the data, obtained differently, on the basis of the same model of preferential solvation.

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