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Analysis of the enthalpies of transfer of Co(II) ion in mixed solvents by means of the theory of preferential solvation

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Abstract

The enthalpies of transfer of Co(II) ion in several aqueous-organic and organic mixed solvents were analysed by means of the theory of preferential solvation. The results provided the quantitative description of preferential solvation of the ion and of its effect on interactions between solvent molecules. They also enabled to compare solvating properties of various mixtures. The analysis revealed a discontinuity in those properties with the composition of the solvent, caused by the changes in the solvent structure. The mean number of molecules of one component of the mixture in the solvation sphere of Co(II) ion versus solvent composition was determined.

Keywords: Enthalpies of transfer; Cobalt(II) ion; Mixed solvents; Preferential solvation theory

1. Introduction

It is well established that first-row transition metal(II) ions of Mn−Zn series exist in water and organic donor solvents, except of those very bulky, as hexasolvated species of pseudooctahedral symmetry. For cobalt(II) ion, which is a subject of the present study, such surrounding predicted by ligand field theory was evidenced from visible absorption spectra in various solvents [1]. Coordination number equal to six was confirmed by nmr studies in water [2], methanol (MeOH) [3], acetonitrile (AN) [4] and *N*,*N*-dimethylformamide (DMF) [5]. The octahedral arrangement of solvent molecules around the central ion was found by using X-ray diffraction in water [6] and by X-ray absorption spectroscopy in *N*,*N*-dimethylformamide [7,8], *N*,*N*-dimethylacetamide (DMA) [8], methanol [9], acetonitrile [10], dimethylsulfoxide (DMSO) [10] and water [11]. The number of solvent molecules in the first solvation sphere of Co(II) ion was also determined on the basis of Raman spectra in DMF and DMA [12].

In binary solvents cobalt(II) ion forms mixed solvation complexes $[Co(L_1)_n(L_2)_{6-n}]^{2+}$ (L_1 and L_2 denote molecules of the solvent components), which kind and concentration vary with the solvent composition. Such complexes were observed in nmr spectra of solutions of Co(II) ion in MeOH−H_2O [3] and MeOH−DMF mixtures [13] and were revealed by analysis of visible absorption spectra of the ion in several aqueous and non-aqueous mixtures [14]. Generally, the mean composition of the solvation sphere differs from that of mixed solvent, so the ion is preferentially solvated by one of the solvent components. Although the studies of divalent transition metal ions in mixed solvents are of growing interest, relatively little is known about the composition of the solvation sphere. It was determined over the whole or partial range of solvent composition on the basis of nmr spectra for Co(II) ion in aqueous DMF [15], for Ni(II) ion in aqueous DMSO [15,16], aqueous MeOH [16] and in MeOH−DMF mixtures [17], whereas for Cu(II) ion in aqueous DMSO and AN [18]. IR spectra were used for resolving the problem for Cu(II) and Zn(II) ions in aqueous acetonitrile [19,20]. Lately, individual component solvation numbers were obtained for ions of Mn−Zn series in DMF−DMA mixtures by using Raman spectroscopy,

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clearly confirming the total solvation number equal to six [12,21,22].

In contrast to spectroscopy methods, the thermodynamic ones do not describe the solvation on the molecular level. Detailed studies of preferential solvation of cobalt(II) ion in a number of aqueous and non-aqueous mixtures were performed on the basis of the enthalpies of transfer of the ion from pure to mixed solvent [23,24]. Two main contributions to the enthalpies of transfer were considered: one of them reflecting changes in the solute–solvent interactions and the other changes in the solvent–solvent interactions with the solvent composition. The qualitative analysis of the variation of the enthalpies of transfer showed that solvation properties of mixed solvents can be strongly modified by interactions between solvent molecules.

Considerable insight into solvation phenomena studied from thermodynamic data provided a theory of preferential solvation presented for the first time in 1983 by de Valera et al. [25]. The model of preferential solvation takes into account, apart from the solute–solvent interactions, also interactions between solvent molecules from the first and further solvation spheres of the solute as well as those in the bulk solvent. Based on the model, the authors derived an equation for the enthalpies of transfer of the solute from pure to mixed solvent, containing three parameters which characterize the solvation in mixtures and have clear physical meaning. The parameters, determined using the experimental enthalpies of transfer, are the measure of preferential solvation and of effect of the solute on the solvent structure, making possible to compare quantitatively solvating abilities of various systems.

The theory was successfully tested in a range of binary mixed solvents for many solutes: electrolytes, like alkali metals [25,26], silver [26] and tetraalkilammonium halides [27,28] as well as non-electrolytes [29–34]; the results were reviewed by Waghorne in 1993 [35]. So far the theory has not been applied to single ions.

This paper presents the analysis of the enthalpies of transfer of cobalt(II) ion, performed on the basis of the preferential solvation theory. The ionic enthalpies of transfer were determined previously from the experimental enthalpies of transfer of appropriate salts, using an extra-thermodynamic TATB (or TPTB) assumption [23,24]. The analysis was carried out for five aqueous-organic mixtures: H_2O-AN, $H_2O-MeOH$, H_2O-DMF, H_2O-DMA and $H_2O-DMSO$ and for two non-aqueous mixtures: AN−DMSO and AN−MeOH. For each system such set of model parameters was found, which ensured the best fitting of calculated and experimental data. The parameters provided valuable information about the energy and structure of the solvation sphere of the ion.

As a final result of the analysis, the mean composition of the first solvation sphere of cobalt(II) ion depending on the solvent composition was calculated. This kind of data was in domain of spectroscopy rather than thermochemical studies.

2. Experimental

Enthalpies of transfer of Co(II) ion from pure to mixed solvents were obtained basing on experimental enthalpies of solution of crystal salts of Co(II), measured over the whole range of solvent composition [24,36–39]. Perchlorate and trifluoromethanesulfonate were used, ensuring lack of ion pair formation in solutions at low salt concentrations. Final concentrations of Co(II) ion did not exceed 5×10^{-3} mol dm^{-3}. No concentration dependence of the enthalpies of solution was found within the experimental scatter, so the mean values of two−three measurements reproducible to 0.3 J mol^{-1} (optionally 0.5 J mol^{-1}) at each solvent composition were treated as the standard enthalpies of solution. Details of experimental conditions were given in Ref. [24]. All measurements were performed at 298.15 K.

Enthalpies of solution of Co(II) perchlorate, forming well-defined solid solvates, were converted to the enthalpies of transfer of $Co(ClO_4)_2$ from pure to mixed solvent in a way described in Ref. [36]. Enthalpies of transfer of anhydrous trifluoromethanesulfonate of Co(II) were calculated simply as the difference of standard enthalpies of solution in mixed and pure solvent.

The splitting of the enthalpies of transfer of salts into ionic contributions was performed on the basis of TATB (or TPTB) assumption. Enthalpies of transfer of the salts taking part in the TATB procedure were measured in $AN-H_2O$ [40] and AN−DMSO mixtures [38], whereas in the remaining systems the enthalpies of solution of sodium perchlorate or trifluoromethanesulfonate were measured and the enthalpies of transfer of Na(I) ion were taken from literature [23,24].

The enthalpies of transfer of salts and of Na(I) ion were approximated by polynomials; the standard deviation did not exceed the value of 0.2 kJ mol^{-1} for Co(II) salts and of 0.05 kJ mol^{-1} for the other salts. The ionic enthalpies of transfer were determined from the interpolated values of proper salts for mole fractions of mixture component changing of 0.05. Resulting uncertainty of the enthalpies of transfer of Co(II) ion determined on TATB assumption was thus about 0.5 kJ mol^{-1}.

3. Calculations

The enthalpies of transfer of a solute from pure solvent A to the mixture of A and B, $\Delta_t H^\circ$, derived from the model of preferential solvation, are as follows [25]:

$$\Delta_t H^\circ = \frac{p x_B}{x_A + p x_B} \Delta\Delta H^\circ_{12} - \frac{\alpha n + \beta N}{x_A + p x_B}(x_A L_A + p x_B L_B) + \frac{p x_B}{x_A + p x_B}(\alpha n + \beta N)\left(\Delta H^*_A - \Delta H^*_B\right) \quad (1)$$

where x_A, x_B are the mole fractions of the components A and B in the mixed solvent, respectively, L_A, L_B the relative partial molar enthalpies of A and B in the mixed solvent, respectively, and ΔH^*_A, ΔH^*_B the enthalpies of condensation of pure components.

Eq. (1) contains three parameters having the physical meaning: (i) an index of preferential solvation of the solute, p, (ii) a composite parameter, $(\alpha n + \beta N)$, being a measure of the net effect of the solute on the solvent structure, and (iii) $\Delta\Delta H^\circ_{12}$, reflecting the relative strength of the solute–solvent bonds in the reorganized pure solvents. The parameter p, defined as

$$p = \frac{n_B x_A}{n_A x_B} \qquad (2)$$

where n_A and n_B are the numbers of molecules A and B in the first solvation sphere of the solute, is a direct measure of the preferential solvation: $p < 1$ denotes that the solute is preferentially solvated by component A, $p > 1$ that the preference is for solvent B. The first term of $(\alpha n + \beta N)$ parameter is connected with the formation of a cavity in the solvent by the solute and the second one reflects the change in solvent bonds between the first and further solvation spheres. The value of $(\alpha n + \beta N)$ is positive if the solvent–solvent interactions are weaken by the solute and is negative if there is a net strengthening of these interactions. $\Delta\Delta H^\circ_{12} = (\Delta H^\circ_{12})_B - (\Delta H^\circ_{12})_A$ is positive if solvation interactions including component A are stronger.

Relative partial molar enthalpies were measured calorimetrically for both components in AN–DMSO system [38] and for water in the aqueous-organic mixtures [36,39,41]; values of L for the organic component of the mixtures were calculated using the Gibbs-Duhem equation. L_{AN} and L_{MeOH} in AN–MeOH mixtures were taken from the literature [26,42,43]. Enthalpies of vaporization (kJ mol^{-1}) of the solvents used were [44]: 43.99 (H_2O), 37.43 (MeOH), 32.94 (AN), 46.89 (DMF), 50.24 (DMA) and [45]: 52.88 (DMSO). All the data refer to 298.15 K.

The solvation parameters were determined in the way described in the literature [28]. Eq. (1) was rearranged to Eq. (3):

$$\frac{(x_A + p x_B)\,\Delta_t H^\circ}{p x_B} = [\Delta\Delta H^\circ_{12} + (\alpha n + \beta N)(\Delta H^*_A - \Delta H^*_B)] - (\alpha n + \beta N)\left(\frac{x_A}{p x_B} L_A + L_B\right) \qquad (3)$$

which expresses the dependence of $(x_A + p x_B)\Delta_t H^\circ / p x_B$ against $(x_A L_A / p x_B + L_B)$. For the correct value of p, Eq. (3) represents a straight line, with a slope $-(\alpha n + \beta N)$ and intercept $\Delta\Delta H^\circ_{12} + (\alpha n + \beta N)(\Delta H^*_A - \Delta H^*_B)$.

The value of p was changed gradually until the best linearity between variables was reached; the remaining model parameters were calculated from the slope and intercept. Using the adjusted values of parameters, the enthalpies of transfer were calculated from Eq. (1). The program computing above quantities was written for x_A changing by 0.05.

4. Results

Solvation parameters for Co(II) ion in the mixtures containing acetonitrile are collected in Table 1 and those in the mixtures of water with strong organic donors in Table 2. The results of the analysis for methanol–water mixtures are presented in Table 3.

In all mixtures studied the experimental enthalpies of transfer could not be reproduced over the entire range of solvent composition using one set of solvation parameters; the satisfactory agreement between calculated and experimental values was found by means of two sets of parameters characteristic for high content of each component. The fitting of calculated and experimental enthalpies of transfer of cobalt(II) ion in the mixtures studied is shown in Figs. 1–3.

Taking into account the well-defined first solvation sphere of Co(II) ion, its composition was calculated from Eq. (2), using the values of parameter p for appropriate regions. Fig. 4 presents the mean number of molecules of one of the solvent components in the solvation sphere of the ion for various mole fractions of this component in the mixture.

Table 1
Solvation parameters for Co(II) ion in mixtures including acetonitrile

System	p	$(\alpha n + \beta N)$	$\Delta\Delta H^\circ_{12}$ (kJ mol^{-1})
Acetonitrile-rich region			
AN–DMSO	32 ± 1	20.2 ± 0.7	−459 ± 14
AN–H_2O	18 ± 1	8.8 ± 0.5	−142 ± 5
AN–MeOH	8 ± 1	8.3 ± 1.7	−73 ± 6
Region of low acetonitrile content			
AN–DMSO	4.0 ± 1.0	29 ± 8	−540 ± 150
AN–H_2O	1.2 ± 0.1	88 ± 6	−970 ± 70
AN–MeOH	1.0 ± 0.1	16 ± 1	−117 ± 2

Table 2
Solvation parameters for Co(II) ion in mixtures of water with organic donor solvent

System	p	$(\alpha n + \beta N)$	$\Delta\Delta H^\circ_{12}$ (kJ mol^{-1})
Region of low water content			
DMF–H_2O	1.4 ± 0.2	−20.7 ± 0.4	10.8 ± 1.1
DMA–H_2O	2.5 ± 1.0	−12.0 ± 0.2	−8.4 ± 1.3
DMSO–H_2O	1.0 ± 0.5	−12.0 ± 0.3	−30.8 ± 2.5
Water-rich region			
DMF–H_2O	0.77 ± 0.06	20.5 ± 1.7	279 ± 25
DMA–H_2O	0.33 ± 0.05	10.3 ± 1.5	207 ± 25
DMSO–H_2O	0.37 ± 0.08	9.2 ± 1.9	203 ± 45

Table 3
Solvation parameters for Co(II) ion in methanol–water mixtures

MeOH–H_2O	p	$(\alpha n + \beta N)$	$\Delta\Delta H^\circ_{12}$ (kJ mol^{-1})
Methanol-rich region	2.1 ± 0.2	−33.4 ± 2.0	326 ± 18
Water-rich region	2.9 ± 0.4	16.9 ± 0.6	−12 ± 8

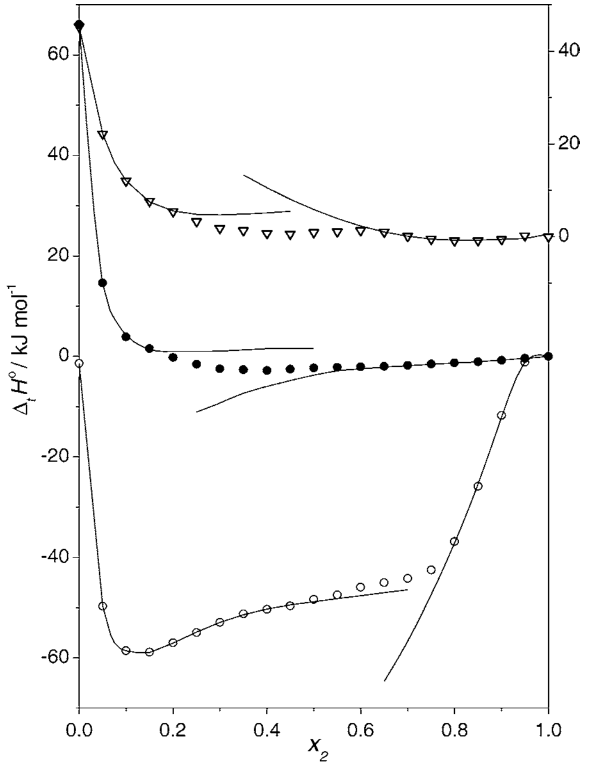

Fig. 1. Enthalpies of transfer (kJ mol^{-1}) of Co(II) ion from pure solvent to its mixtures with acetonitrile at 298.15 K: experimental (points); calculated from Eq. (1) (solid lines). (●) AN−DMSO; (○) AN−H_2O; (▽) AN−MeOH (right-side scale).

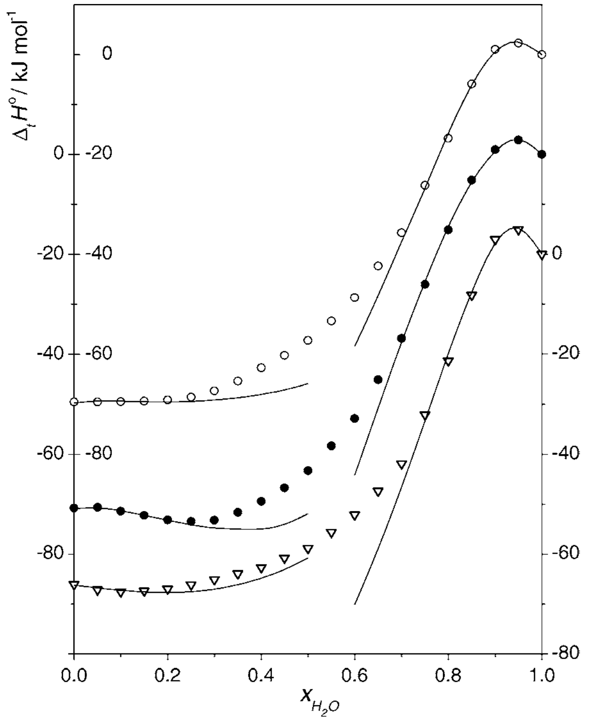

Fig. 2. Enthalpies of transfer (kJ mol^{-1}) of Co(II) ion from water to aqueous-organic mixtures at 298.15 K: experimental (points); calculated from Eq. (1) (solid lines). (○) DMSO−H_2O (inner left-side scale); (●) DMF−H_2O (outer left-side scale); (▽) DMA−H_2O (right-side scale).

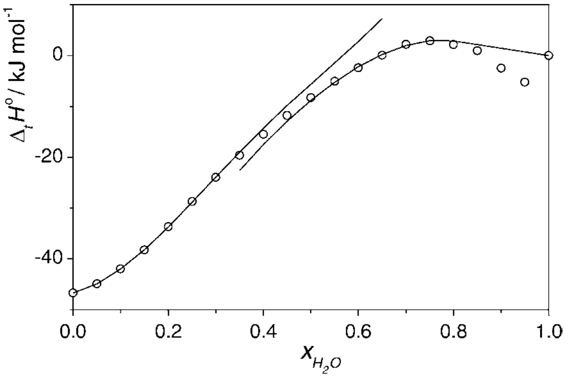

Fig. 3. Enthalpies of transfer (kJ mol^{-1}) of Co(II) ion from water to MeOH−H_2O mixtures at 298.15 K: experimental (points); calculated from Eq. (1) (solid lines).

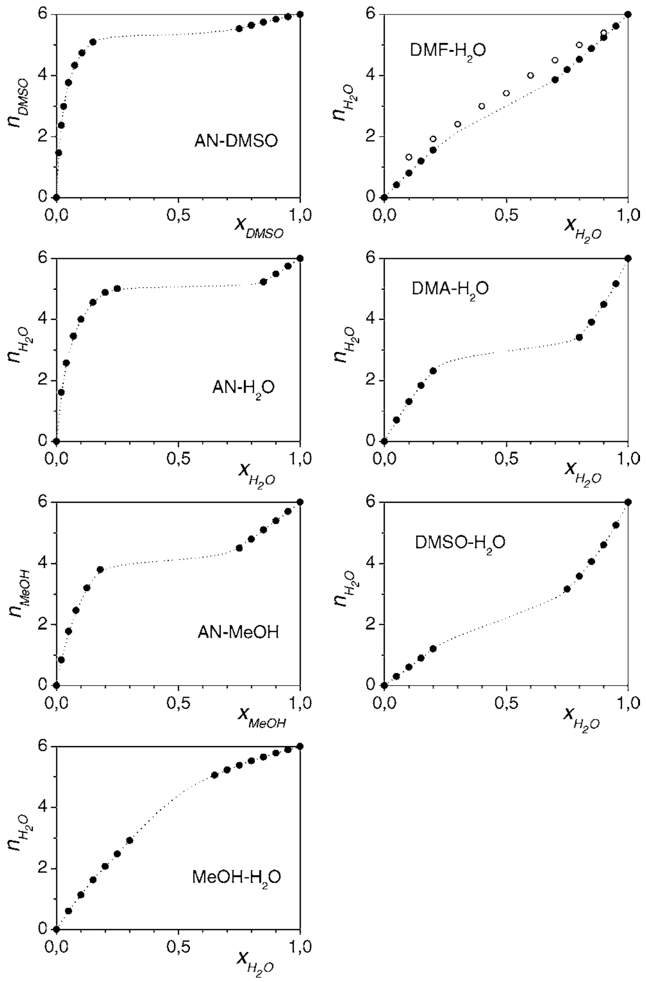

Fig. 4. The mean number of molecules of one of the components in the solvation sphere of Co(II) ion for various mole fractions of this component in the mixture: (●) calculated from Eq. (2); (○) determined from pmr spectra [15].

5. Discussion

5.1. Systems including acetonitrile

The common feature of the mixtures including acetonitrile is the preferential solvation of Co(II) ion by the second component in the region of its low content. The index of preferential solvation, *p*, is the highest for AN–DMSO system, for which electron donor properties of the components differ most markedly (Lewis basicity of solvent molecules, expressed by Gutmann donor numbers, DN, is as follows [46,47]: AN (14.1) < H_2O (18.0) < MeOH (19) < DMSO (29.8)).

The sequence of the preferential solvation index is the same as that of $\Delta\Delta H^{\circ}_{12}$ parameter, what suggests that the preferential solvation results mainly from differences in interactions of Co(II) ion with molecules of both components. Different values of $\Delta\Delta H^{\circ}_{12}$ parameter for AN–H_2O and AN–MeOH systems, despite of the similar donicity of water and methanol molecules, could be explained by the different structure of the second solvation sphere of the ion. Each water molecule from the first solvation sphere is able to bond two water molecules in the second solvation sphere, whereas the coordinated methanol molecule can bond ony one molecule. The strengthening of ion–solvent interactions resulting from cooperation of hydrogen bonds is thus more effective in AN–H_2O mixtures.

In all three systems the Co(II) ion causes the net weakening of interactions between solvent molecules, what is revealed by positive values of $(\alpha n + \beta N)$ parameter. It is especially evident in AN–DMSO system, in which DMSO molecules coordinated to the ion cannot bond other solvent molecules. The lower values of $(\alpha n + \beta N)$ in the two remaining systems show that the enthalpy effect of cavity formation is highly compensated by enhanced interactions in the second and further solvation spheres.

The index of preferential solvation found for the second component-rich region indicates that the acetonitrile content in the solvation sphere of the ion is almost negligible in AN–DMSO system, whereas it is very closed to that in the bulk solvent in AN–MeOH and AN–H_2O systems. The latter, rather unexpected result seems to arise from the special structure of the water-rich mixtures with gaps in the water network occupied by acetonitrile molecules. The strong arrangement of this structure arround the Co(II) ion may promote acetonitrile molecules to its coordination sphere [14]. The increase in the $(\alpha n + \beta N)$ values compared with those for acetonitrile-rich region results from the stronger interactions between molecules of the second component. It is particularly seen in AN–H_2O system with the water net structure. Thus, the contribution of the structural effects to the enthalpies of transfer in this region is more significant than in acetonitrile-rich solutions.

5.2. Organic donor solvent–water mixtures

In the organic component-rich region there is a slight preferential solvation of cobalt(II) ion by water, despite of the much stronger donor properties of organic solvents (Gutmann donor numbers of DMF, DMA and DMSO are 26.6, 27.8 and 29.8, respectively [45]). The negative values of $(\alpha n + \beta N)$ reveal the strengthening of solvent–solvent interactions caused by the ion. The both effects may be explained by hydrogen bonds formed between water and organic component: the water molecule interacting with one or two organic molecules becomes the stronger electron donor and replaces organic component in the first solvation sphere of the ion. As a result, hydrogen bonds between coordinated water molecules and organic molecules strengthen. The explanation is also supported by relatively small values of $\Delta\Delta H^{\circ}_{12}$ in this region. Differentiation of solvation parameters in the three systems arises from different basicity of organic components; in DMA–H_2O system the steric hindrance in coordination of DMA molecules to Co(II) ion should be additionally taken into account, what justifies the most pronounced preference of water.

In the water-rich region cobalt(II) ion is preferentially solvated by the organic component; the preference is, however, not so strong as could be expected from the difference in donor properties of organic solvent and water molecules. The latter, being in the solvation sphere, show the increased donor ability, because they interact with further molecules via hydrogen bonds, whereas coordinated organic molecules have not such possibility.

The positive values of $(\alpha n + \beta N)$ for the systems indicate that the net effect of cobalt(II) ion is to break solvent–solvent bonds: the strengthening of the solvent interactions around the coordination sphere is outweighed by their breaking associated with the formation of a cavity. This effect is, however, much weaker than in AN–H_2O system, in which acetonitrile molecules are not able to form strong hydrogen bonds. Those between water and DMF, DMA or DMSO molecules partly disrupt the net structure of water, thus facilitating the cavity formation, while acetonitrile molecules, filling gaps in the water network make it even more difficult. Besides, the hydrogen bonds between water molecules from the solvation sphere of the ion with amide/dimethylsulfoxide molecules become additionally stronger because of co-operativity mechanism.

5.3. Methanol–water system

Cobalt(II) ion is preferentially hydrated over the whole range of solvent composition, the analysis recovered as well two different structural regions of the mixture. Negative value of $(\alpha n + \beta N)$ parameter in the methanol-rich region indicates that the resultant effect of the ion on the solvent interactions is to strengthen them. Thus the preference of water arises from the formation of two hydrogen bonds by coordinated water molecule, while that of methanol is able to form only one such bonding. The net increase in the solvent–solvent interactions is more noticeable (the value of $(\alpha n + \beta N)$ is more negative) than in the analogous region of aqueous mixtures of aprotic DMF, DMA and DMSO, in which organic molecules solvating the ion cannot form hydrogen bonds.

In the water-rich region the preference of water increases considerably because of the larger enhancement of water structure around the ion. The net effect of the ion on solvent–solvent bonds is, however, to break them, because the enthalpy contribution connected with the cavity formation outweighs that from the strengthening of solvent bonds in the solvation sphere, what results in the positive value of $(\alpha n + \beta N)$ parameter.

As can be seen from Fig. 3, the enthalpies of transfer calculated in the region of very high water content do not fit the experimental ones: no set of reasonable solvation parameters allowed to approximate the local minimum on the enthalpies of transfer curve. It may reflect the complex changes of the solvent structure in this region, resulting from the balance between hydrophobic and hydrophilic hydration of methanol (e.g. the recent studies of H_2O–MeOH system suggest disordering of water structure around methyl group of methanol [48], in contrary to the prevailing opinion about its enhancement). Another explanation involves some doubts as to validity of TATB assumption, used for the splitting of the enthalpies of transfer of salts into ionic contributions in aqueous alcohols [23].

5.4. *Comparison with spectroscopy results*

The composition of the solvation sphere of Co(II) ion recovered from the analysis of the enthalpies of transfer is to a high degree consistent with that from spectroscopy studies. For comparison, the results obtained on the basis of pmr spectra of Co(II)–DMF–H_2O solutions are shown in Fig. 4 [15]. The almost constant composition of the Co(II) solvation sphere in the broad range of intermediate solvent composition in AN–H_2O system was also found for Zn(II) ion from infrared measurements [20]. Preferential solvation of Co(II) ion was studied by visible spectra of solvation complexes in the mixtures including acetonitrile as well as in aqueous methanol and dimethylsulfoxide [14]. Results of the factor analysis of the spectra are compatible with those reported in this work. For example, they confirm the presence of acetonitrile in the solvation sphere of Co(II) ion even at low content of acetonitrile in its mixtures with water and methanol.

The values of preferential solvation index p in aqueous-organic mixtures correspond well with donor properties of water in various solvents, derived from infrared spectra [49]. Effective (real) donor number of water molecules in bulk water was found as 26.7, very closed to that of DMF molecule, what can justify only slight preference of DMF in the water-rich region and less than expected preference of DMA and DMSO. The value of DN for water in DMSO environment is almost equal to that for DMSO, in accordance with lack of preferential solvation of Co(II) ion in DMSO-rich region. Also donor number of water diluted in acetonitrile, enhanced from 18 for separate molecule to 23 in acetonitrile environment, fits to the strong preference of water in AN-rich solutions.

6. Summary

The applying of the preferential solvation theory of Waghorne to the enthalpies of transfer of Co(II) ion provided valuable information about the energetic and structural aspects of its solvation. Specially, it was possible to determine the mean composition of the first solvation sphere and the extent to what the solvent structure is reorganized by the ion. The separation of two main contributions to the overall enthalpies of transfer was particularly useful in the systems with strong solvent–solvent interactions which can mask changes in the solvation sphere and make the qualitative interpretation of $\Delta_t H^\circ$ versus composition profiles difficult.

The model parameters, describing the solvation in mixed solvents quantitatively, enabled to draw a comparison between various mixtures with regard to the molecular properties of their components.

The analysis revealed a break in the solvating abilities of mixed solvents: separate sets of the model parameters were obtained for the regions of high content of each component. Discontinuity in those abilities at intermediate solvent compositions can be explained by a change in the solvent structure from that characteristic for one of the component to that of the other.

The analysis was performed for cobalt(II) ion with strong solvation interactions and well-defined coordination sphere, what makes it a convenient subject for solvation studies. The break in the solvation properties, observed in aqueous as well as in non-aqueous solvent systems, indicates that the enthalpies of transfer of Co(II) ion are a very sensitive probe of the solvent structure.

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