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THE HYDROPHOBIC EFFECT IN AQUEOUS SOLUTIONS OF POSITIONAL ISOMERS OF ALKAN-*n*-OLS. A CALORIMETRIC STUDY AT 298.15 K

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ABSTRACT

Enthalpies of dilution were measured for binary aqueous solutions of positional isomers of pentanol and hexanol, and for some ternary solutions containing two of the following alcohols: methanol, ethanol, propan-1-ol, butan-1-ol, and pentan-1-ol. The enthalpic interaction coefficients found depend greatly on the alkyl chain length and on the position of the hydroxyl functional groups. A refinement of the model of overlapping hydration cospheres is proposed. Two hydrated molecules should interact through a preferential, "side on", orientation, stabilized by the contemporaneous juxtaposition of the hydroxyl groups and the alkyl chains. The effects which cause the h_{xx} values of positional isomers to differ are discussed.

INTRODUCTION

Non-bonding interactions, hydrophobic interactions among them, can be studied through the virial coefficients of the power series of the excess thermodynamic properties expressed as a function of molalities [1]. For instance, the pairwise, self and cross, enthalpic coefficients, which can be easily obtained from the enthalpies of dilution of the corresponding binary or ternary solutions of the solutes under examination [2–6], are very useful in that they give information on the changes in state of the solvent released upon the interaction between hydrated molecules, and thus on the nature of the hydration cosphere [2,7–11].

Extensive studies on mono- and polyhydroxylated compounds have unravelled the influence of the position and stereochemistry of the functional groups, [1,2,4,7–13]. A better insight into the non-bonding interactions in these solutions has been obtained by means of a group additivity approach, [3]. This allows information to be obtained on the contributions made by the

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groups into which a molecule can be arbitrarily divided to the overall pairwise coefficients. The limitation of this approach, however, are clearly revealed when dealing with configurational [7] or positional [4] isomers and with stereoisomers [14–20]. This method, in fact, cannot distinguish between isomers, notwithstanding the large differences between the enthalpic interaction coefficients of these substances.

Recently, some of us have proposed a different model for the interaction of positional isomeric diols [4]. The aim of the present work is to extend this model to the isomeric positional alkan-*n*-ols studied here and to their mixtures, and to test its validity and its predictive capability for these solutes. For these reasons, the heats of dilution in water of binary aqueous solutions of pentan-1-ol, pentan-2-ol, pentan-3-ol, hexan-1-ol, hexan-2-ol and hexan-3-ol have been measured at 298.15 K. Moreover, the heats of dilution of ternary aqueous solutions containing methanol (or ethanol) and propan-1-ol, butan-1-ol and pentan-1-ol have also been obtained, and the corresponding enthalpic interaction coefficients evaluated.

EXPERIMENTAL

Alkan-*n*-ols (Aldrich, Carlo Erba and Fluka products) were of the highest purity commercially available, and they were used without further purification.

Measurements of heats of dilution were performed by means of an LKB 10700-1 standard flow microcalorimeter, using procedures described previously [2,4–6].

RESULTS

The enthalpy change that occurs upon dilution of a solution containing *n* solutes is related to the corresponding excess enthalpy and to the pairwise and higher order coefficients

$$\begin{aligned}\Delta H_{\text{dil}}(\bar{m}^i \rightarrow \bar{m}^f) &= H^{\text{E}}(\bar{m}^f) - (m_x^f/m_x^i) H^{\text{E}}(\bar{m}^i) \\ &= \sum \sum h_{xy} m_x^f m_y^f - (m_x^f/m_x^i) \sum \sum h_{xy} m_x^i m_y^i \\ &\quad + \text{higher terms} \qquad (1)\end{aligned}$$

where m_x^i, $m_y^i, \ldots, m_x^f$, $m_y^f \ldots$, are the molalities of each solute and $\bar{m}^i = \Sigma m_x^i$, $\bar{m}^f = \Sigma\, m_x^f$ are the osmolalities before and after the dilution process. The units of the enthalpy change are expressed in J kg^{-1} of solvent. Usually, an auxiliary function $\Delta H^{n\star}$ is used [20], which is the difference between the enthalpy of dilution of a solution containing n solutes and the sum of the enthalpies of dilution of the solutions containing each solute

$$\Delta H^{n\star} = \Delta H_{\text{dil}}(\overline{m}) - \sum \Delta H_{\text{dil}}(m_x) \tag{2}$$

where $\overline{m}$ is the osmolality of the solutions. For ternary systems the auxiliary function is given by

$$\begin{aligned}\Delta H^{**}(x, y) &= \Delta H_{\text{dil}}(x, y) - \Delta H_{\text{dil}}(x) - \Delta H_{\text{dil}}(y)\\ &= 2h_{xy}m_x^f\left(m_y^f - m_y^i\right) + \text{higher terms}\end{aligned} \tag{3}$$

The heats of dilution of binary solutions are obtained from

$$\begin{aligned}\Delta H_{\text{dil}} &= H^{\text{E}}(m^f) - (m^f/m^i)H^{\text{E}}(m^i)\\ &= h_{xx}m^f(m^f - m^i) + h_{xxx}m^f(m^{f2} - m^{i2}) + \text{higher terms}\end{aligned} \tag{1$'$}$$

where m^f and m^i are the final and initial molalities, respectively.

In Table 1 the enthalpic interaction coefficients for all the alkan-n-ols examined, together with their own 95% confidence limits, are reported. It is to be noted that the heat of dilution of hexan-1-ol was nil up to the solubility limit (ca. 0.01 m). In the same table the h coefficients for some alkan-n-ols reported in the literature are also given [2,21–23]. All the coefficients are positive, increasing with increasing alkyl chain length, and they depend markedly on the position of the –OH functional group along the carbon atom backbone. For instance, the h_{xx} values for the two

TABLE 1

Enthalpic interaction coefficients for binary aqueous solutions of alkan-n-ols at 298.15 K

Alkan-n-ol	h_{xx} [a]	h_{xxx} [b]
Methanol [c]	218	
Ethanol [d]	243 (10)	65 (5)
Propan-1-ol [d]	559 (14)	158 (8)
Propan-2-ol [e]	339	
Butan-1-ol [d]	1003 (15)	646 (56)
Butan-2-ol [f]	916	
Pentan-1-ol	1766 (68)	
Pentan-2-ol	1502 (113)	1666 (543)
Pentan-3-ol	1290 (125)	1549 (301)
Hexan-1-ol	$\Delta H_{\text{dil}} = 0$	
Hexan-2-ol	2064 (88)	
Hexan-3-ol	2224 (112)	

[a] Units: J kg mol^{-2}.
[b] Units: J kg^2 mol^{-3}.
[c] Ref. 21.
[d] Ref. 2.
[e] Ref. 22.
[f] Ref. 23. The figures in parentheses represent the 95% confidence indices.

TABLE 2

Enthalpic interaction coefficients for ternary aqueous solutions of the mixtures of alkan-1-ols reported below, at 298.15 K

System	h_{xy} [a]	h_{xxy} [b]	h_{xyy} [b]
MeOH–EtOH	264 (6)		
MeOH–PrOH	328 (6)		
MeOH–BuOH	406 (12)		
MeOH–PeOH	580 (25)		
EtOH–PrOH [c]	372		
EtOH–BuOH [c]	464		
EtOH–PeOH	701 (51)		
PrOH–BuOH [c]	748		
PrOH–PeOH	998 (44)		
BuOH–PeOH	1303 (80)	621 (49)	2759 (428)

[a] Units: J kg mol^{-2}.

[b] Units J kg^2 mol^{-3}.

[c] Ref. 2. The figures in parentheses are the 95% confidence limits. Legend: MeOH, methanol; EtOH, ethanol; PrOH, propan-1-ol; BuOH, butan-1-ol; PeOH, pentan-1-ol.

positional isomers hexan-3-ol and hexan-2-ol differ by about 150 J kg mol^{-2}, and by about 500 for pentan-1-ol and pentan-3-ol. A larger difference was found between the h_{xx} values for the two isomeric diols hexane-1,2-diol and hexane-2,5-diol (about 1200 J kg mol^{-2}) [4].

In Table 2 the enthalpic cross interaction coefficients are given for the ternary systems examined in the present study, together with those for other systems from the literature [2]. As can be seen from Table 2, for some systems, notwithstanding the limited range of concentrations explored, triplet interaction coefficients were needed to get the best fit. Obviously, in these cases, the 95% confidence limits on the coefficients were higher than those relating to other systems requiring only one coefficient to obtain the best fit of the experimental data. It would be possible to improve the confidence limit by performing a very large number of experimental data at higher concentrations. However, the aim of this work was to determine the pairwise interaction coefficients: we have thus not tried to minimize the error on the triplet coefficients.

DISCUSSION

The surprisingly large differences in the thermodynamic behaviour of the aqueous solutions of positional isomers of polyhydroxylated compounds, and the inadequacy of the model of the statistical overlap of the hydration cospheres commonly used to describe them, has recently led some of us to propose a new, simple model for the non-bonding interactions in aqueous solutions of alkane-*n*,*m*-diols [4].

The model relies on the hypothesis that a most probable orientation of a pair of interacting molecules exists in water: this orientation allows the best juxtaposition of the hydrated –OH functional groups and, contemporaneously, of the hydrophobically hydrated alkyl chains. Hence, for these linear diols the OH–OH and CH_2–CH_2 forcing action determines a "side on" most probable orientation [24]. This hypothesis is supported not only by thermodynamic but also by spectroscopic studies. In fact, studies of the nuclear relaxation times of D_2O solutions of hexane-1,2-diol and propane-1,2-diol have shown a small but systematic decrease of the relaxation time for the C-4 and C-5 of hexane-1,2-diol and, contemporaneously, those for C-1 and C-2 of propane-1,2-diol, when they are present in a ternary solution relative to the relaxation times obtained for the respective binary solutions [25]. This model permits a simple explanation of the differences in the h_{xx} values for the different isomers, when a factorization of the effects contributing to the "side on" orientation has been attempted. Assuming that these substances are in the trans-planar conformation, the OH–OH interaction in the "side on" orientation causes the CH_2 groups in the α-position relative to the carbon atom bearing the functional –OH group and this same CH_2 bearing the –OH group to occupy remote positions: the overlap of these groups is less effective than that of other hydrated alkyl groups in the molecule. Hence, the enthalpic interaction coefficients decrease with an increasing number of α-CH_2 groups, thus discriminating between differential positional isomers. Taking into account this effect, and considering the total number of CH_2 groups, a unifying empirical representation was proposed plotting the pair enthalpic coefficients as a function of a complex abscissa which contains contributions due to the total number of carbon atoms, to the α carbon atoms and to those bearing hydroxyl groups. A linear trend was obtained for all the diols known, in agreement with the hypothesis that the coefficients depend on the number of α-CH_2 groups. However, it is important to underline that this "side on" orientation is only one of those most probable, not the unique one.

The proposed model is here applied to the series of alkan-*n*-ols presently under study. As shown in Fig. 1, a plot of the h coefficients versus the third power of n_{CH_2} for alkan-1-ols from methanol to pentan-1-ol, including also the cross coefficients relative to the mixtures of alkan-1-ols, gave a linear trend, thus indicating that the CH_2–CH_2 interaction is more than statistical, and rather a "forced" interaction. In contrast, the CH_2–OH interaction is negligible, and this is an indication that for normal alkanols also the "side on" orientation is one of the most probable. For the ternary systems, the number of equivalent CH_2 groups, n_{CH_2}, is computed as the arithmetic mean of the number of the CH_2 equivalent of the two molecules. In the same figure, the h coefficients relative to alkane-1,2-diols are also reported: again a linear trend is obtained, with a larger slope and an intercept double that for the alkan-1-ols. This finding indicates the simultaneous interaction

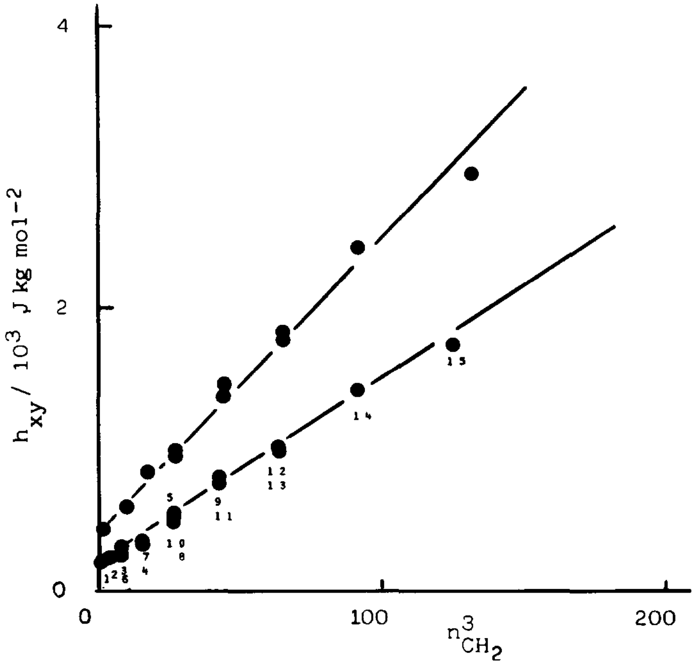

Fig. 1. Self and cross enthalpic interaction coefficients for binary and ternary aqueous solutions of alkan-1-ols (lower line) and alkane-1,2-diols (upper line) versus the third power of the number of equivalent CH_2 groups, $n^3_{CH_2}$. For the ternary systems, n_{CH_2} is equal to half the sum of the total number of the equivalent CH_2 groups. The legend for alkan-1-ols is (1) MeOH-MeOH; (2) MeOH-EtOH; (3) MeOH-PrOH; (4) MeOH-BuOH; (5) MeOH-PeOH; (6) EtOH-EtOH; (7) EtOH-PrOH; (8) EtOH-BuOH; (9) EtOH—PeOH; (10) PrOH-PrOH; (11) PrOH-BuOH; (12) PrOH-PeOH; (13) BuOH-BuOH; (14) BuOH-PeOH; (15) PeOH-PeOH.

of the two -OH groups for the diols, which leads to a different degree of overlap of the hydrophobic regions. Thus, it can be concluded that diols behave more hydrophobically than alkanols, namely in a more cooperative manner.

Moreover, an analysis of the enthalpic pairwise coefficients of the binary and ternary solutions of alkan-1-ols through the Savage and Wood group contribution approach (SWAG) supported the conclusions just arrived at. This approach assumes that every group of a molecule x interacts statistically with every group of a molecule y, independently of the position of the interacting groups in the molecules [3]. The enthalpic pairwise coefficient is then given by

$$h_{xy} = \sum \sum (n_i)_x (n_j)_y \{H_{ij}\}$$

where $(n_i)_x$ and $(n_j)_y$ are the number of i and j groups on the molecules x and y, respectively, and $\{H_{ij}\}$ is the enthalpic contribution of an i–j

TABLE 3

Group contributions $\{H_{ij}\}$ (J kg mol^{-2}) to the pair enthalpic coefficients for alkan-1-ols at 298.15 K

Fitting I			Fitting II		
ij	CHOH	CH_2	ij	CHOH	CH_2
CHOH	91 (135)	0.42 (40)	CHOH	92 (41)	–
CH_2	0.42 (40)	61 (13)	CH_2	–	61 (4)

Fitting II is obtained by neglecting the CHOH/CH_2 contribution, which in Fitting I has no physical meaning. The figures in parentheses are the 68% confidence limits.

interaction. In Table 3 the values obtained for $\{H_{ij}\}$ are reported: they indicate that the cross contribution CH_2–CHOH is meaningless (Fitting I), and that a better fit is obtained when the interpolating function contains only the contributions due to the CHOH–CHOH and CH_2–CH_2 interactions (Fitting II). It is interesting to point out that the same conclusions were drawn from the free energy parameters, which led to the neglect of the cross interaction ($g_{\text{CHOH-CHOH}} < 0$; $g_{\text{CH}_2\text{-CH}_2} < 0$; $g_{\text{CH}_2\text{-CHOH}} > 0$) [12].

We decided to test whether the unifying representation is also possible in the case of alkan-*n*-ols. In Fig. 2 the pair, self and cross, enthalpic interaction coefficients for the alkan-*n*-ols under examination are plotted versus the complex abscissa $N = n_{\text{CH}_2}(n_{\text{CH}_2} - n_{\alpha\text{CH}_2})(n_{\text{CH}_2} - n_{\text{CH}_2\text{(OH)}})$. To evaluate this abscissa, it must be remembered that n_{CH_2} is the number of equivalent CH_2 groups in the alkyl chain, computed assuming –OH is the functional group, $n_{\alpha\text{CH}_2}$ is the number of equivalent CH_2 groups in a position α to a functional –OH group, and $n_{\text{CH}_2\text{(OH)}}$ is the number of equivalent CH_2 groups bearing functional –OH groups. A CH_2 group is taken as 1, $CH \equiv 0.5CH_2$ and $CH_3 \equiv 1.5CH_2$ [3]. Again a linear trend is obtained, as for diols, thus indicating the validity of the "side on" model also for alkanols. This is a very interesting and encouraging result, because it is evidence that this orientation is possible even in the presence of only one –OH "forcing" group. The result underlines the major role of the contemporaneous overlap of the hydrophobic–hydrophobic and hydrophilic–hydrophilic regions.

Finally, it is worth stressing that a similar interpretation has been proposed in explaining chiral recognition in water between the D and L stereoisomers of α-aminoacids [14,20]. In this case, the differences between the homotactic (h_{DD} or h_{LL}) and heterotactic (h_{DL}) coefficients are imposed by the favourable electrostatic interaction between the zwitterions of the two interacting amino acids. Another case which could be described by this model is that of *myo*-inositol [9]. This six-membered cyclic polyol has five equatorial hydroxyl groups, and it exhibits the behaviour of a typical structure breaking solute, being characterized by negative values of the

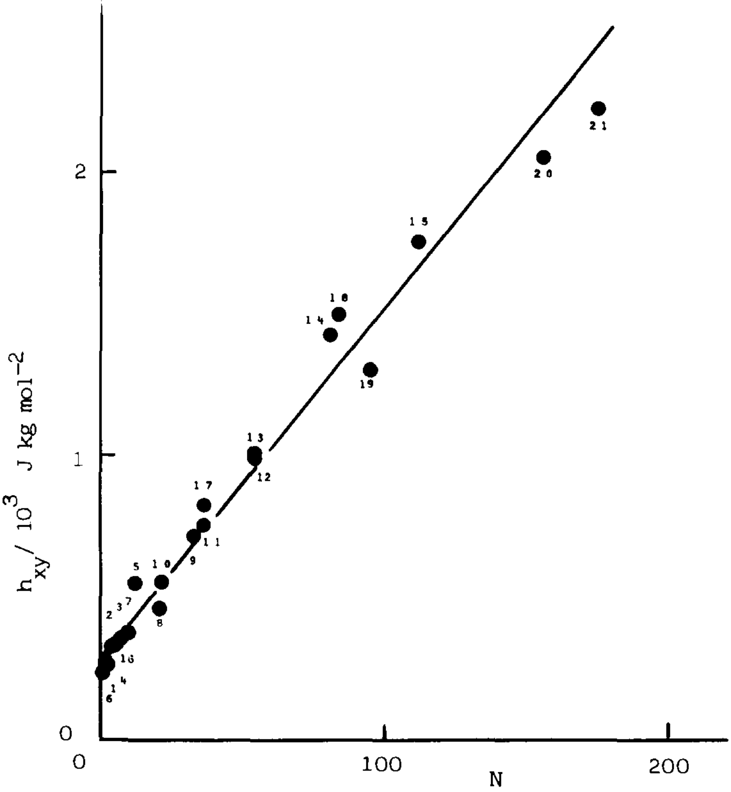

Fig. 2. Self and cross enthalpic interaction coefficients for binary and ternary solutions of alkan-*n*-ols versus $N = n_{CH_2}(n_{CH_2} - n_{\alpha CH_2})(n_{CH_2} - n_{CH_2(OH)})$; n_{CH_2} = number of equivalent CH_2 groups in the alkyl chain; $n_{\alpha CH_2}$ = number of equivalent CH_2 groups in position α to a functional –OH group; $n_{CH_2(OH)}$ = number of equivalent CH_2 groups bearing functional –OH groups. For the ternary systems, n_{CH_2} is half the sum of the total number of the respective CH_2 groups. Numbering is as in Fig. 1 up to 15. For the other systems reported, the legend is (16) 2PrOH–2PrOH; (17) 2BuOH–2BuOH; (18) 2PeOH–2PeOH; (19) 3PeOH–3PeOH; (20) 2HeOH–2HeOH; (21) 3HeOH–3HeOH.

enthalpic and free energy coefficients ($h_{xx} = -800$ and $g_{xx} = -260$ J kg mol^{-2}). The highly negative value of h_{xx}, very different from that of other polyols having linear chains of six carbon atoms, could be explained in terms of a prevailing interaction between the hydroxyl groups of two molecules. In fact, the equatorial position should favour the juxtaposition of five –OH groups, competing with the interaction between the hydrophobic carbon atoms on the backbone. This leads to minor positive contributions to the enthalpic interactions coefficients.

As a conclusion, the study of aqueous solutions of alkanols and diols is proving very fruitful, in that it allows refinement of the model of overlapping hydration cospheres, supplying further information on the non-bonding interactions in these solutions.

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