Thermochimica Acta, 206 (1992) 43–54
Elsevier Science Publishers B.V., Amsterdam

A model for the interaction between hydrophilic and hydrophobic solutes – aqueous solutions containing biuret or urea and hydroxylated substances

G. Castronuovo, R.P. Dario, C. Della Volpe and V. Elia
Department of Chemistry, University "Federico II", Naples (Italy)

(Received 22 October 1991)

Abstract

Enthalpies of dilution of ternary aqueous solutions containing biuret or urea and alkan-1-ols, alkan-1,2-diols and alkan-1,2,3-triols have been determined at 298.15 K by means of a flow microcalorimeter. The cross pairwise coefficients of the virial expansion of the excess enthalpies were determined. These coefficients are positive and depend in a complex manner on the length of the alkyl chain of the alkanols. The behaviour of these systems was interpreted in terms of preferential interactions between hydrophilic groups and of repulsive interactions between hydrophobic and hydrophilic groups.

INTRODUCTION

Weak, non-bonding interactions are important in many biological processes: their change or disruption, for instance, may lead to the collapse of the native form of a protein. Among the weak, non-bonding interactions occurring in aqueous solutions, the hydrophobic interaction has been widely studied, especially with regard to protein stability. Until recently, it was widespread opinion that hydrophobic interactions are the most important driving force for many biochemical processes. However, some doubts have been raised about the major importance of this interaction [1–4]. Most probably, hydrophilic interactions, which are highly dependent on orientation and on the properties of the solvent, are as important as hydrophobic ones in highly specific processes, such as protein folding and molecular recognition.

Studies from this laboratory, concerning thermodynamic and spectroscopic properties of alkan-*m*,*n*-diols [5–8], alkan-*m*-ols [9] and α-amino-acids [10–12], have shown the importance of hydrophilic–hydrophilic interactions. A model has been proposed, through which it was possible to

---

Correspondence to: V. Elia, Department of Chemistry, University "Federico II", Via Mezzocannone 4, 80134 Naples, Italy.

explain differences in the interactions between positional isomers or stereoisomers that cannot be explained using usual statistical approachs [13]. This interaction model, in fact, demonstrates that two hydrated molecules of an alkanol interact through a preferential orientation stabilized by the interaction between hydrophilic groups [5]. This makes the juxtaposition and the interaction between hydrophobic groups more effective: the cooperativity shown for a homologous series is higher than that predicted by a purely statistical model. A very important, successful result of our model lies in the possibility of explaining "chiral recognition". In fact, on these bases, two hydrated molecules of α-aminoacids in their zwitterionic forms interact preferentially via electrostatic interactions, suggesting the existence of two "sociated" molecules. These are very different for the interaction between the side chains, depending on whether the two molecules have the same or different chirality [10–12].

Pairwise enthalpic coefficients of the virial expansion of the excess enthalpies are particularly useful for obtaining information about the interaction mechanism. It should be remembered that the physical meaning of the pair interaction coefficient of an excess property is linked to the variation of the thermodynamic property when two hydrated molecules are brought from an infinite distance, where solute–solvent interactions prevail, to a finite distance where solute–solute, water-mediated interactions are operating. The success obtained in correlating the enthalpic coefficients with the –OH position on the molecule, with the alkyl chain length and with chiral recognition, suggested that we should extend these studies to molecules having different effects on the structure of water. On the basis of the signs and values of the enthalpic, entropic and free energy coefficients, non-electrolytes have been classified as [14,15] (1) hydrophobic structure-makers: $g_{xx} < 0$ and $Ts_{xx} > h_{xx} > 0$; (2) hydrophilic structure-breakers: $g_{xx} < 0$ and $h_{xx} < Ts_{xx} < 0$; (3) hydrophilic structure-makers: $g_{xx} > 0$ and $h_{xx} > Ts_{xx} > 0$.

In the present paper, a study is presented of the interaction between solutes belonging to the first two classes. Enthalpies of dilution of ternary aqueous solutions of alkan-1-ols, alkan-1,2-diols and alkan-1,2,3-triols in the presence of biuret, urea, or glycine were measured and enthalpic cross-interaction coefficients are evaluated. The aim of this work is to verify that the hypothesis of a preferential orientation also holds for the solutes studied here, by examining the various types of interactions between the chaotropic [16] agent and the hydroxylated substances.

EXPERIMENTAL

Biuret, urea and glycine were Carlo Erba (Milano) and Serva products, and the alkanols were purchased from a different source (Sigma or Aldrich). They were of the highest purity commercially available.

Solutions were prepared by weight and solutes were dried in vacuo above P_2O_5.

Measurements of the heats of dilution were carried out in the usual way by means of an LKB flow microcalorimeter. Experimental details are reported in the literature [5,13,17–20].

THERMODYNAMIC RELATIONS

Virial coefficients of the power series of the excess enthalpies as a function of the molalities can be easily derived from the enthalpies of dilution of solutions containing n solutes and from the enthalpies of dilution of the respective binary solutions. The enthalpy change that occurs upon a dilution process

$$\left[\sum_x n_x \text{ moles of } x + A \text{ kg of solvent}\right] + [B \text{ kg of solvent}]$$
$$= \left[\sum_x n_x \text{ moles of } x + (A+B) \text{ kg of solvent}\right] \tag{1}$$

is related to the corresponding excess enthalpy

$$\begin{aligned}\Delta H_{dil}(\text{J kg}^{-1}) &= H^{\text{E}}(\overline{m}^{\text{f}}) - [A/(A+B)]H^{\text{E}}(\overline{m}^{\text{i}})\\ &= H^{\text{E}}(\overline{m}^{\text{f}}) - (m_x^{\text{f}}/m_x^{\text{i}})H^{\text{E}}(\overline{m}^{\text{i}})\end{aligned} \tag{2}$$

where $\overline{m}^{\text{f}}$ and $\overline{m}^{\text{i}}$ are the osmolalities of solutions after and before the dilution process, respectively, $\overline{m} = \Sigma_x m_x$ and $A/(A+B) = m_1^{\text{f}}/m_1^{\text{i}} = m_2^{\text{f}}/m_2^{\text{i}} = \ldots$. Substituting relations between excess enthalpies and virial coefficients into eqn. (2) gives

$$\Delta H_{\text{dil}}(\text{J kg}^{-1}) = \sum_x \sum_y h_{xy} m_x^{\text{f}} m_y^{\text{f}} - (m_x^{\text{f}}/m_x^{\text{i}})\left[\sum_x \sum_y h_{xy} m_x^{\text{i}} m_y^{\text{i}}\right] + \ldots \tag{3}$$

Knowing the self coefficient h_{xx} for each solute, it is possible to determine the cross coefficients h_{xy} by means of the auxiliary function ΔH^{n*} [12]

$$\Delta H^{n*} = \Delta H_{\text{dil}}(\overline{m}^{\text{i}} \to \overline{m}^{\text{f}}) - \sum_x \Delta H_{\text{dil}}(m_x^{\text{i}} \to m_x^{\text{f}}) \tag{4}$$

which depends only on the cross coefficients.

In the case of ternary solutions, eqn. (4) reduces to

$$\begin{aligned}\Delta H^{**} &= \Delta H_{\text{dil}}(\overline{m}^{\text{i}} \to \overline{m}^{\text{f}}) - \Delta H_{\text{dil}}(m_x^{\text{i}} \to m_x^{\text{f}}) - \Delta H_{\text{dil}}(m_y^{\text{i}} \to m_y^{\text{f}})\\ &= 2h_{xy} m_x^{\text{f}}(m_y^{\text{f}} - m_y^{\text{i}}) + \text{higher terms}\\ &= 2h_{xy} m_y^{\text{f}}(m_x^{\text{f}} - m_x^{\text{i}}) + \text{higher terms}\end{aligned} \tag{5}$$

A least-squares procedure was used to determine the h_{xy} coefficients. Only

TABLE 1

Enthalpic cross-interaction coefficients (J kg mol^{-2}) for binary and ternary aqueous solutions containing alkan-1-ols and urea (U), glycine (G) or biuret (BU) at 298.15 K

Alkan-1-ols	h_{xx}	h_{xy}(U)	h_{xy}(G)	h_{xy}(BU)
Methane-1-ol	215 [a]	201 ± 5	377 ± 13	419 ± 15
Ethane-1-ol	243 ± 10 [b]	319 ± 9 [d]	553 ± 12 [e]	652 ± 7 [e]
Propane-1-ol	559 ± 14 [b]	425 ± 5 [d]	654 ± 6 [f]	858 ± 11 [e]
Butane-1-ol	1003 ± 15 [b]	476 ± 8 [d]	799 ± 10 [f]	1048 ± 17 [e]
Pentane-1-ol	1766 ± 68 [c]	500 ± 50	810 ± 71	1055 ± 34

[a] Ref. 21. [b] Ref. 18. [c] Ref. 9. [d] Ref. 22. [e] Ref. 23. [f] Ref. 24. The self-interaction coefficients of the chaotropic agents are −350 [13], −447 [25] and −2120 [26] J Kg mol^{-2} for urea, glycine and biuret, respectively.

pairwise coefficients were found to be necessary for the best-fitting of the experimental data, owing to the limited range of concentration explored.

RESULTS

Table 1 gives the cross coefficients for ternary solutions containing biuret (BU), urea (U), or glycine (G), and alkan-1-ols. These coefficients

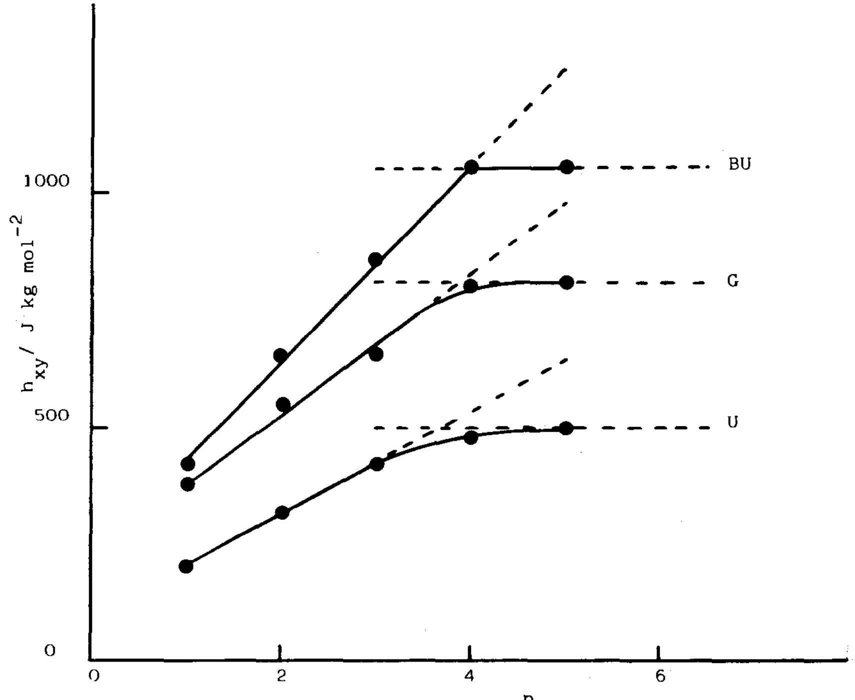

Fig. 1. Plots of enthalpic cross-interaction coefficients h_{xy} vs. the number of carbon atoms of alkan-1-ols n_C for the ternary alkan-1-ols–urea (U), alkan-1-ols–glycine (G) and alkan-1-ols–biuret (BU) systems.

TABLE 2

Enthalpic cross-interaction coefficients (J kg mol^{-2}) for binary and ternary aqueous solutions containing alkan-1,2-diols and urea (U) or biuret (BU) at 298.15

Alkan-1,2-diols	h_{xx}	h_{xy}(U)	h_{xy}(BU)
Ethane-1,2-diol	415 ± 30 [a]	46 ± 2 [e]	63 ± 12
Propane-1,2-diol	589 ± 1 [b]	195 ± 28	252 ± 24
Butane-1,2-diol	923 ± 5 [c]	380 ± 20	536 ± 22
Pentane-1,2-diol	1777 ± 30 [d]	350 ± 26	512 ± 43
Hexane-1,2-diol	2955 ± 55 [d]	438 ± 36	617 ± 37

[a] Ref. 27. [b] Ref. 17. [c] Ref. 28. [d] Ref. 5. [e] Ref. 13.

are positive and depend either on the chaotropic action of the destructuring agent (BU, U, or G), or on the alkyl chain length. As can be seen from Fig. 1, for all systems, a maximum, invariant value of the enthalpic coefficients was reached at $n_C = 4$, n_C being the number of carbon atoms of the alkanol. The cross coefficients for the ternary solutions containing BU are higher than those for solutions containing G or U.

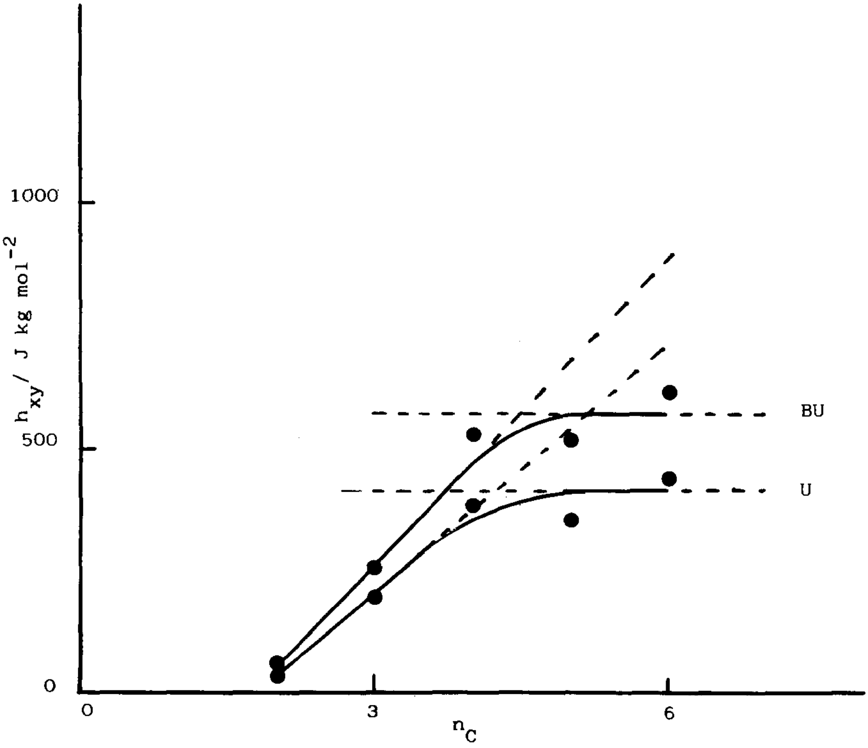

Fig. 2. Plots of enthalpic cross-interaction coefficients h_{xy} vs. the number of carbon atoms of alkan-1,2-diols n_C for the ternary alkan-1,2-diols–urea (U) and alkan-1,2-diols–biuret (BU) systems.

TABLE 3

Enthalpic cross-interaction coefficients (J kg mol^{-2}) for binary and ternary aqueous solutions containing alkan-1,2,3-triols and urea (U) or biuret (BU) at 298.15 K

Alkan-1,2,3-triols	h_{xx}	h_{xy}(U)	h_{xy}(BU)
Propane-1,2,3-triol	251 [a]	29 ± 18 [b]	−126 ± 10 [c]
Hexane-1,2,3-triol	1678 ± 66	364 ± 61	512 ± 53
Heptane-1,2,3-triol	2879 ± 54	448 ± 50	507 ± 51

[a] Ref. 13. [b] Ref. 38. [c] Ref. 14.

Table 2 lists the cross coefficients for ternary solutions containing biuret or urea as destructuring agent and alkan-1,2-diols. As with the alkan-1-ols, the cross coefficients for solutions containing biuret are higher than those of urea-containing systems, although there is a decrease in the difference between their values. As shown in Fig. 2, for these systems the maximum, invariant value was attained at $n_c \geq 5$.

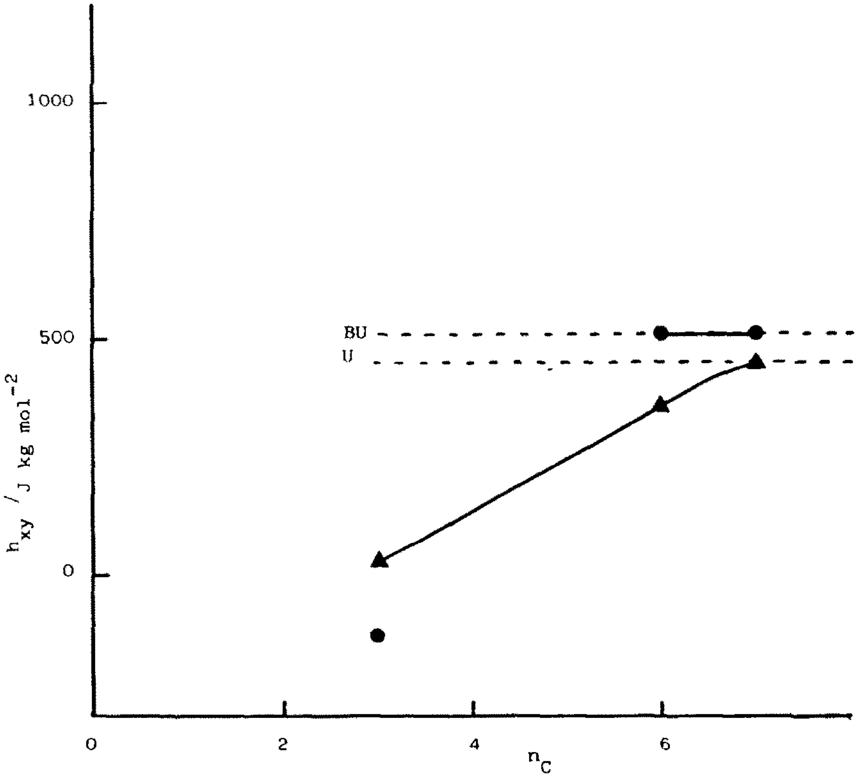

Fig. 3. Plots of the enthalpic cross-interaction coefficients h_{xy} vs. the number of carbon atoms of alkan-1,2,3-triols n_C for the ternary alkan-1,2,3-triols–urea (U) and alkan-1,2,3-triols–biuret (BU) systems.

Table 3 reports the enthalpic self-interaction coefficients for the binary aqueous solutions containing propane-, hexane- and heptane-1,2,3-triols. The h_{xx} values are positive, and they increase with increasing alkyl chain length. The table also shows the cross-interaction coefficients for the ternary systems containing the same triols and urea or biuret. The trends are the same as for the homologous series of alkan-1,2-diols (see Fig. 3). However, because of the limited number of triols available, it was impossible to determine at which number of carbon atoms the plateau begins. As with the two preceding cases, the increase in the cross coefficients for the urea-containing systems is much smoother, from which it can be inferred that the plateau begins at $n_c \geq 6$.

DISCUSSION

In recent years, a clear, though qualitative, understanding of the non-bonding interactions in aqueous solutions of non-electrolytes has been reached from the analysis of the excess thermodynamic properties using the Savage and Wood group-additivity approach (SWAG) [13]. As is often stressed, however, this approach does not account for the large differences in the thermodynamic parameters concerning positional isomers or stereoisomers, or for the enhanced cooperativity of hydrophobic interactions of polyhydroxylated compounds. However, according to this approach, interactions between groups can be characterized as

(i) Favourable interactions between hydrophilic groups
$(G_{\text{hydrophilic-hydrophilic}} < 0)$

(ii) Favourable interactions between hydrophobic groups
$(G_{\text{hydrophobic-hydrophobic}} < 0)$

(iii) Unfavourable interactions between hydrophilic and hydrophobic groups
$(G_{\text{hydrophilic-hydrophobic}} > 0)$

where G is the group contribution to the pairwise coefficient of the virial expansion of the excess free energy [29]. Then, the interactions between like groups are favoured, while mixed interactions are prevented by a positive contribution to the free energy. Making use of these results, and attempting to overcome the rigid, statistical SWAG approach, the occurrence can be hypothesized of some more probable orientations in solution between two hydrated molecules (model of preferential orientation) [5,7,8]. These orientations are made possible by the juxtaposition of similar groups, while groups having a different action on the structure of water tend to stay far away.

The first application of this model rationalized successfully the experimental data concerning the interactions in aqueous solutions of α-amino-

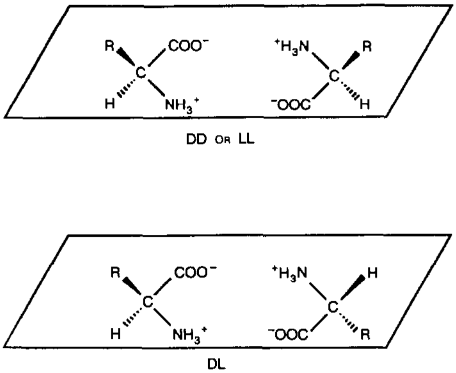

Fig. 4. Schematic representation of the interaction between two molecules of an α-aminoacid. In the upper part, the two molecules have the same chirality: the two side chains lie in the same half-space. In the lower part, the two molecules have different chirality: the two alkyl groups lie in two different half-spaces. This is, of course, an extreme situation and many other cases must necessarily exist.

acids [10–12]. Among the various favourable configurations of two "sociated" molecules of the same or different chirality, the interaction between the charged groups of the zwitterion is supposed to prevail. In this case, the cooperativity of the hydrophobic interaction was very low, the enthalpic coefficients showing a linear dependence on the number of carbon atoms. The two "sociated" molecules show large differences toward the interaction between the hydrophobic groups of the side chains, depending on their chirality. In fact, when the chirality of the two interacting aminoacids is the same, the side chains are in the same half-space determined by the interactions between the charged groups. In contrast, for molecules of different chirality, the alkyl groups lie in two different half-spaces (see Fig. 4). Thus, these two different orientations, enhancing the steric differences of the two interacting solutes, lead to rather large differences in the interactions between side chains, thus making chiral recognition possible. The homotactic enthalpic interaction coefficient then becomes more positive than the heterotactic interaction because of the stronger interactions between the hydrophobic domains of the side chains of the α-aminoacids ($H_{\mathrm{CH_2-CH_2}} > 0$). Accordingly, chiral recognition is not possible when the cause of this preferential orientation disappears [11], i.e. the presence of the zwitterion. In 1 M HCl, a new preferential orientation prevails: the "side on" [30], determined by the simultaneous juxtaposition of the alkyl and carboxyl groups, making the steric differences between two "sociated" molecules very small. However, the cooperativity of the hydrophobic interaction is higher, the enthalpic coefficients showing a quadratic dependence on the number of carbon atoms [12].

In the case of the self-interaction between polyol molecules, as the number of OH groups increases, their configurational sequence determines the values of the pairwise coefficients. For sorbitol, dulcitol and perseitol, whose hydrophilic and hydrophobic domains are well separated [31], the h_{xx} values change sign, passing from positive to negative. When the OH groups, for their configurational sequence, are bound on the same side with respect to a trans-planar conformation, a competition may exist between the two possible preferential configurations. The one stabilized by hydrophilic–hydrophilic interactions seems to prevail, as indicated by the negative sign of h_{xx}. For more complex sequences of hydrophilic and hydrophobic domains, intermediate h_{xx} values appear. In the extreme case of myo-inosytol, a cyclic hexanol with five equatorial OH groups, the highest negative value of h_{xx} (-800 J kg mol^{-2}) is obtained [32]. For monosaccharides, however, small, positive values of the enthalpic and free energy pair coefficients denote more complex systems [33], probably because the steric hindrance of the OH groups distances the carbon skeleton and because of their particularly stable hydration cage [34]. When the molecules of the solute have well-separated hydrophilic and hydrophobic domains (mixed solutes such as alcohols), the simultaneous juxtaposition of domains having the same action on the structure of water results in an enhanced cooperativity of the hydrophobic interaction, the enthalpic coefficients showing a dependence on the third power of the number of carbon atoms [5].

The model of preferential configuration has allowed even the complex behaviour of positional isomers of polyhydroxylated substances to be rationalized. Using other approaches reported in the literature, the difference in the pair enthalpic coefficients of positional isomers of alkan-*m*-ols [9] and alkan-*m*,*n*-diols [5,7] remained unexplained. The starting hypothesis implies a preferential orientation, according to which two “sociated” molecules juxtapose the maximum number of hydrophilic and hydrophobic groups, minimizing interactions between hydrophilic and hydrophobic domains. On these bases, a linear correlation was found between the pair enthalpic coefficients and a complex abscissa function. This abscissa takes into account the total number of equivalent CH_2 groups and the number of carbon atoms which, in a “side on” configuration, occupy remote positions. For the alkan-1,2,3-triols examined here, namely propane-, hexane- and heptane-1,2,3-triol, the enthalpic self-interaction coefficients are equal to or less than the self-coefficients of the respective 1,2-diols having a carbon atom less (ethane-1,2-, pentane-1,2- and hexane-1,2-diol). The equality of the coefficients could indicate that one of the three –OH functional groups is inactive in a “side on”, preferential orientation, probably because it is in a remote position with respect to the juxtaposition. The same happens for the CH_2 groups in the α-position to the carbon atoms bearing the two interacting OH groups. The values of the enthalpic coefficients of the three triols examined, reported as a function of the complex abscissa

$$N = n^{\mathrm{t}}_{\mathrm{CH_2}}\left(n^{\mathrm{t}}_{\mathrm{CH_2}} - n^{\alpha}_{\mathrm{CH_2}}\right)\left(n^{\mathrm{t}}_{\mathrm{CH_2}} - n^{\mathrm{OH}}_{\mathrm{CH_2}}\right)$$

fall on the same line obtained for alkan-*m*,*n*-diols [7]. This also confirms the hypothesis of a "side on" orientation for these triols.

The reliability of the model in predicting the enthalpic pair coefficient also held for the cross interaction of alkan-1-ols and alkan-1,2-diols of different alkyl chain length [7]. For these systems, a linear correlation between the enthalpic cross coefficients and the complex abscissa function was only found if the number of equivalent CH_2 groups was taken as the half-sum of the overall CH_2 groups on the two molecules. The need to use the half-sum could be justified by the involvement of the whole alkyl-chain through a partial folding of the longer alkyl-chain on the shorter one.

The success of the model of preferential interaction in rationalizing the experimental values of the enthalpic pair coefficients for the systems involving like substances, has led us to extend it to the cross interactions between solutes having a different action on the structure of water. In earlier papers from this laboratory, data have been reported concerning ternary aqueous solutions of urea, thirourea or biuret and linear polyols, $CH_2OH(CHOH)_nCH_2OH$ $(0 \leq n \leq 5)$ [14,35], or monosaccharides [22,23, 36,37]. The negative values of the cross coefficients were interpreted as owing to the preferential interaction between the hydrophilic domains of the polyhydroxylated compounds with the hydrophilic groups of the structure-breaking solute. The consequent, prevailing release of destructured water to the bulk determines the sign of the coefficient. This agrees well with the present point of view on these types of interactions, in that the role of the favourable (hydrophilic–hydrophilic) interactions are prevalent in determining the overall value of the pair coefficient. In the case of the cross interaction between structure-breaking and structure-making solutes belonging to the first class (alcohols), a prevailing release of structured water from the hydrophobic cospheres occurs, yielding positive values for the h_{xy} coefficients. Thus, the values of the cross coefficients are expected to increase with increasing chaotropic action of the structure breaker and with increasing alkyl chain length of the hydrophobic solute. Unfortunately, the literature data concern solutes whose alkyl chains are too short (up to butan-1-ol) to enable clear information on the role played by the latter parameter to be obtained. Therefore, we were forced to study cross interactions between structure-breaking solutes and the higher alkan-1-ols, the complete series of alkan-1,2-diols and some alkan-1,2,3-triols. For all series, whatever the structure breaker used, a common trend is found. The cross coefficients increase linearly with increasing number of carbon atoms in the alkanols, until a plateau is reached. For alkan-1-ols, the values of the cross coefficients depend greatly on the structure-breaking capability of the chaotropic agent. The plateau is reached at $n_c \geq 4$ for all three series (Fig. 1). For alkan-1,2-diols, the h_{xy} values depend slightly on the nature of the hydrophilic solute, the plateau being reached at $n_c \geq 5$. For alkan-1,2,3-triols, the limited data do not permit a conclusive discussion on the critical value of the number of carbon atoms. The two h_{xy} values for the systems containing biuret are the same for hexane- and heptane-1,2,3-triols, whereas for systems with urea, they are still increasing: the plateau could be at $n_c \geq 6$. The unique trend of h_{xy} versus the number of carbon atoms of the alkanols interacting with different structure-breaking solutes, can be rationalized using the model of preferential orientation. Favourable, hydrophilic–hydrophilic interactions between the hydroxyl groups of the alkanol and one of the hydrophilic groups of biuret, urea or glycine, determine a more probable orientation of the two interacting hydrated molecules. This is to be expected because the preferential orientation depends prevailingly on the juxtaposition of the hydrophilic groups, the hydrophobic ones pointing away from the hydropyhilic solute. In this preferential orientation, the maximum number of carbon atoms that can interact is determined neither by the length of the chaotropic agent, nor by the length of the alkyl chain of the alkanol. A critical length of the alkyl chain of the hydrophobic solute must be operating: above that, the hydrophilic domain of the structure breaker cannot extend its disruptive action. Thus, it seems that the hydrophilic head of the alkanols behaves as a whole, independently of the number of hydroxyl groups. The structure-breaking solute interacts with this hydrophilic head, probably extending its action over three CH_2 groups. This could be the reason why the plateau for alkan-1-ols is reached at $n_c \geq 4$, for alkan-1,2-diols at $n_c \geq 5$, and for alkan-1,2,3-triols at $n_c \geq 6$. The smoother trend of the coefficients for those systems involving urea could be an indication of a minor stability of the pair of "sociated" molecules. The major stability for the systems containing biuret could be attributed to the presence of more hydrophilic groups on the molecule of the destructuring agent and, then, to the increased probability of favourable interactions.

In conclusion, information concerning pair molecular processes have indicated the fundamental role of hydrophilic–hydrophilic interactions. In earlier papers, we have demonstrated an enhanced cooperativity of hydrophobic interactions as a result of a preferential orientation stabilized by hydrophilic interaction. Here, one of the contributions is missing, in that the structure-breaking solute has only hydrophilic groups. This implies only a partial involvement of the alkyl chain of the alkanols, which is followed by a plateau. As a consequence, contributions from the various interactions to the interaction coefficients are different in binary and ternary solutions: therefore, correlations between self- and cross-interaction coefficients must be used with care, unless the same mechanism is known to operate in binary and ternary solutions.

ACKNOWLEDGMENTS

We thank F. Racioppoli for performing some of the calorimetric experiments. This work was financially supported by the Ministry of University and Scientific Research (MURST), Rome.

REFERENCES

1 A. Ben-Naim, J. Chem. Phys., 90 (1989) 7412.
2 A. Ben-Naim, J. Phys. Chem., 94 (1990) 6893.
3 M. Mezei and A. Ben-Naim, J. Chem. Phys., 92 (1990) 1359.
4 A. Ben-Naim, Biopolymers, 29 (1990) 567.
5 C. Cascella, G. Castronuovo, V. Elia, R. Sartorio and S. Wurzburger, J. Chem. Soc. Faraday Trans. I, 86 (1990) 85.
6 S. Wurzburger, R. Sartorio, V. Elia and C. Cascella, J. Chem. Soc. Faraday Trans. 1, 86 (1990) 3891.
7 S. Andini, G. Castronuovo, V. Elia and L. Fasano, J. Chem. Soc. Faraday Trans. 1, 86 (1990) 3567.
8 L. Ambrosone, S. Andini, G. Castronuovo, V. Elia and G. Guarino, J. Chem. Soc. Faraday Trans. 1, 87 (1991).
9 G. Castronuovo, R.P. Dario and V. Elia, Thermochim. Acta, 181 (1991) 305.
10 G. Barone, G. Castronuovo, P. Del Vecchio, V. Elia and S. Puzziello, J. Solution Chem., 18 (1989) 1105.
11 G. Castronuovo, V. Elia, C. Giancola and S. Puzziello, J. Solution Chem., 19 (1990) 855.
12 G. Castronuovo, V. Elia and M. Magliulo, Can. J. Chem., 69 (1991) 794.
13 J.J. Savage and R.H. Wood, J. Solution Chem., 5 (1976) 731.
14 C. Cascella, G. Castronuovo, V. Elia, R. Sartorio and S. Wurzburger, J. Chem. Soc. Faraday Trans. 1, 85 (1989) 3289.
15 G. Barone, P. Cacace, G. Castronuovo and V. Elia, J. Chem. Soc. Faraday Trans. 1, 77 (1981) 1569.
16 F. Franks, Philos. Trans. R. Soc. London Ser. B, 278 (1977) 33.
17 G. Borghesani, R. Pedriali and F. Pulidori, J. Solution Chem., 18 (1989) 289.
19 F. Franks, M.D. Pedley and S. Reid, J. Chem. Soc. Faraday Trans. I, 72 (1976) 1359.
19 H.L. Friedman and C.V. Krishnan, J. Solution Chem., 2 (1972) 119.
20 J.E. Desnoyers, G. Perron, L. Avedikian and J.P. Morel, J. Solution Chem., 5 (1976) 631.
21 J. Perron and J.E. Desnoyers, J. Chem. Thermodyn., 13 (1981) 1105.
22 G. Barone, G. Castronuovo, P. Del Vecchio and V. Elia, J. Therm. Anal., 34 (1988) 479.
23 G. Barone, G. Castronuovo, P. Del Vecchio, V. Elia and M.T. Tosto, J. Solution Chem., 17 (1988) 925.
24 G. Barone, G. Castronuovo and V. Elia, Adv. Mol. Relaxation Processes (Molecular Liquids), 23 (1982) 279.
25 F.T. Gucker, H.P. Pickard and W.L. Ford, J. Am. Chem. Soc., 62 (1940) 2698.
26 G. Barone, P. Cacace, G. Castronuovo and V. Elia, Can. J. Chem., 59 (1981) 1257.
27 F. Franks and M.D. Pedley, J. Chem. Soc. Faraday Trans. I, 79 (1983) 2249.
28 G. Borghesani, R. Pedriali, F. Pulidori and I. Scaroni, J. Solution Chem., 15 (1986) 397.
29 B.Y. Okamoto, R.H. Wood, P.T. Thompson, J. Chem. Soc. Faraday Trans. 1, 74 (1978) 1990.
30 T.H. Lilley, in G.C. Barret (Ed.), The Chemistry and Biochemistry of Amino Acids, Chapman and Hall, Methuen, 1984, Chapt. 21.
31 G. Barone, B. Bove, G. Castronuovo and V. Elia, J. Solution Chem., 10 (1981) 803.
32 G. Barone, P. Cacace, G. Castronuono and V. Elia, Carbohydr. Res., 119 (1986) 1.
33 G. Barone, P. Cacace, G. Castronuovo and V. Elia, Gazz. Chim. Ital., 112 (1982) 153.
34 A. Suggett, J. Solution Chem., 5 (1976) 33.
35 G. Barone, V. Elia and E. Rizzo, J. Solution Chem., 11 (1982) 687.
36 G. Barone, G. Castronuovo, V. Elia and M.T. Tosto, J. Solution Chem., 15 (1986) 199.
37 G. Barone, G. Castronuovo, P. Del Vecchio and V. Elia, J. Therm. Anal., 34 (1988) 431.
38 V. Abate, G. Barone, G. Castronuovo, V. Elia and E. Rizzo, J. Solution Chem., 12 (1983) 645.