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INTERACTIONS BETWEEN AMINOACIDS AND ALCOHOLS IN WATER AT 25 °C

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The enthalpies of dilution of ternary aqueous solutions containing an alcohol (ethanol, *n*-propanol, *n*-butanol or tert-butanol) and an aminoacid or a peptide (glycine, glycyl-glycine or glycyl-glycyl-glycine), were measured at 25 °C. The results were used to calculate pair cross interaction parameters between solutes. The coefficients of virial expansion of the excess enthalpies are compared with those referring to solutions containing the same alcohols and other structure-breaking solutes (urea, thiourea and biuret). The enthalpic pair parameter for the systems glycine-alcohols shows the same trend, as reported in the literature, for similar structure-breaking solutes, with a maximum in the cross coefficients when reported versus the self pair interaction coefficients of alcohols. The results are interpreted in terms of a prevailing release of water from the cospheres of alcohols.

A great interest is presently devoted to studies concerning the interactions between nonelectrolytes in water. Such an interest is primarily related to the "non-bonding" interactions between model molecules, an approach that has led to relevant contributions to the knowledge of the interactions involving biological macromolecules [1–18]. Hydrophobic interactions are also included in such "non-bonding" types, and for them a great number of studies are reported in the literature and quantitative models are now available [3, 19–23]. Generally speaking, weak interactions can be investigated by determining the second virial coefficients of the power expansion of the excess thermodynamic functions. For unsymmetrical mixtures containing a solvent and one or more solutes, an excess thermodynamic property J is usually defined as;

$$J^E = J - J_1^0 - \sum_{x=2}^{n} m_x \overline{J}_x^0 - J^{ID} \qquad (1)$$

where J^E and J refer to an amount of solution containing 1 kg of solvent and $m_2 \ldots m_n$ moles of solute species; J_1^0 is the standard property of 1 kg of pure solvent, and J_x^0 are the limiting partial molal quantities for each solute; J^{ID} is the part of J due to the ideal mixing of the components of the mixtures. The representation of the experimental excess thermodynamic properties as a power expansion on the scale of

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molalities, was theoretically built on the McMillan Mayer theory of solutions [1–18, 24], giving the following virial expansion:

$$J^E = \sum j_{xy}m_xm_y + \sum j_{xyz}m_xm_ym_z + \ldots \tag{2}$$

that can be explicitated for the Gibbs energy G^E, enthalpy H^E, entropy S^E, volume V^E etc., according to definition (1). For each temperature we proposed to classify non-associating nonelectrolytes into three classes using the sign of the second coefficients of the virial expansions of the excess enthalpy, free energy and entropy of the corresponding binary solutions [13]:

a) Hydrophobic structure-making solutes $g_{xx} < 0; \quad Ts_{xx} > h_{xx} > 0$ (3)

b) Hydrophilic structure-breaking solutes $g_{xx} < 0; \quad h_{xx} < Ts_{xx} < 0$ (3′)

c) Hydrophilic structure-making solutes $g_{xx} > 0; \quad h_{xx} > Ts_{xx} > 0$ (3″)

For the prevailingly hydrophobic solutes the mechanism of the self interaction is explained through the model which supposes the overlap of hydration spheres, which qualitatively takes into account the signs of the second virial coefficients [7, 20–22]. Besides the alcohols [6, 7, 14], examples of this behaviour are very common among the alkyl derivatives of amides [6, 14, 27], ureas [9, 28, 29] and uncharged peptido amides [17, 30–32]. Some of the hydrophilic destructuring or chaotropic solutes are just the head terms of these families of solutes (formamide, urea, etc.). A mechanism of coalescence of the hydration shells was proposed also to explain the properties of this set of solutes [11, 13, 33, 34]. Besides other nonelectrolytes (thiourea, biuret, etc.) the aminoacid glycine and its oligomers [35–41] that exist essentially as dipolar ions, fall in this group.

Since the beloging to one or another family of solutes depends on the degree of alkyl substitutions, there are solutes with an intermediate behaviour such as monomethylurea [11]. It is also possible that some solutes pass from one to another group on changing temperature.

For hydrophilic structuring solutes such model cannot be invoked because of the positive sign of g_{xx}. Recently, we have discussed the properties of these solutes, mostly saccharides [42–44]. However, in explaining the effects involved in the pair interactions, some questions arise that require a deeper insight into the problem. To gain information that enable us to discriminate different mechanisms of interaction for these types of solutes we are carrying on some calorimetric studies, determining the enthalpy of dilution of ternary solutions of combinations of the types of solutes classified before [15, 45–50].

Here is presented a calorimetric study of the interaction involving structure—breaking solutes, such as glycine, and prevailingly hydrophobic solutes, such as alcohols. The results will be expressed in terms of cross pair interaction coefficients of the virial expansion of the excess enthalpies. The study of the interactions between the two classes of compounds are of great interest to a better understanding of the nature of hydrophobic interactions and the stability of hydrophobic cospheres.

Experimental

Materials and methods

Glycine (G), glycyl-glycine (G_2) and glycyl-glycyl-glycine (G_3) (Sigma products) and ethanol (EtOH), *n*-propanol (PrOH), *n*-butanol (*n*BuOH) and *tert*-butanol (*t*BuOH) (Carlo Erba products, spectroscopic grade), were used without further purification. The solutions were prepared by weight from solutes and solvent before each set of measurements. Deionized, double distilled water was used.

The heats of dilution of the ternary aqueous solutions were determined by means of an LKB 10700–1 standard flow microcalorimeter. Experimental details, formalism and treatment of the data are described in preceding papers [9, 11, 13, 15, 16, 45–50].

Results and discussion

The excess enthalpy H^E (m_x, m_y) (J/kg of solvent) for a ternary solution containing m_x moles of solute x and m_y moles of solute y per kg of solvent is defined as:

$$\begin{aligned} H^E(m_x, m_y) &= h(m_x, m_y) - H_w^\theta - m_x\overline{H_x^0} - m_y\overline{H_y^0} = \\ &= h_{xx}m_x^2 + 2h_{xy}m_xm_y + h_{yy}m_y^2 + h_{xxx}m_x^3 + 3h_{xxy}m_x^2m_y + \dots \end{aligned} \tag{4}$$

where H is the enthalpy of the solution, H_w^θ is the standard enthalpy of 1 kg of solvent (water) and $\overline{H_x^0}$ and $\overline{H_y^0}$ the partial molal enthalpy at infinite dilution for the two solutes, h_{xx}, h_{yy} and h_{xy} the self and cross pair interaction coefficients of the virial expansion of the excess enthalpy.

The enthalpy of dilution $\Delta_{\text{dil}}H(x, y)$ of the ternary solution is simply related to the excess enthalpy and finally to the pair cross interaction coefficients by the following relations:

$$\begin{aligned} \Delta_{\text{dil}}H[m_x^i, m_y^i) \rightarrow (m_x^f m_y^f)] &= H^E(m_x^f, m_y^f) - m_y^f/m_y^i H^E(m_x^i, m_y^i) \\ \Delta H^{**} &= \Delta_{\text{dil}}H[(m_x^i, m_y^i) \rightarrow (m_x^f, m_y^f)] - \Delta_{\text{dil}}H(m_x^i \rightarrow m_x^f) - \\ \Delta_{\text{dil}}H(m_y^i \rightarrow m_y^f) &= 2h_{xy}m_x^f(m_y^f - m_y^i) + \dots \end{aligned} \tag{5}$$

Table 1 Heats of dilution of ternary aqueous solutions of glycine (*G*) and alcohols at 25 °C

		G–EtOH		
m_x^f	m_x^i	m_y^f	m_y^i	ΔH^{**}, J/kg
0.1768	0.3620	0.2693	0.5515	−55.6
0.1571	0.3208	0.2393	0.4887	−44.2
0.1421	0.2896	0.2165	0.4413	−35.9
0.1217	0.2479	0.1854	0.3777	−25.7
0.1027	0.2021	0.1156	0.2276	−11.3
0.07835	0.1571	0.1193	0.2393	−10.3
0.07024	0.1421	0.1007	0.2165	− 8.16
0.08518	0.1723	0.09595	0.1941	− 7.78
0.07870	0.1591	0.08865	0.1792	− 6.60
0.07494	0.1514	0.08439	0.1705	− 5.90
0.06023	0.1217	0.09175	0.1854	− 5.26
0.05568	0.1123	0.06273	0.1265	− 3.24
		G–PrOH		
0.09457	0.1930	0.1877	0.3831	−24.4
0.09016	0.1836	0.1790	0.3645	−21.9
0.1170	0.2372	0.1208	0.2451	−19.4
0.08584	0.1745	0.1704	0.3464	−19.3
0.1057	0.2146	0.1092	0.2218	−15.7
0.075677	0.1556	0.1524	0.3088	−15.4
0.06998	0.1420	0.1389	0.2818	−12.9
0.09231	0.1893	0.09540	0.1956	−12.3
0.08013	0.1622	0.08279	0.1676	− 8.92
0.06890	0.1391	0.07123	0.1428	− 6.45
		G–*t*BuOH		
0.1009	0.2063	0.2088	0.4269	−35.3
0.09136	0.1867	0.1890	0.3863	−29.0
0.08021	0.1634	0.1660	0.3382	−21.9
0.06820	0.1386	0.1412	0.2869	−16.4
0.07914	0.1601	0.08730	0.1766	−10.9
0.05353	0.1085	0.1107	0.2244	−10.2
0.07548	0.1527	0.08324	0.1684	−10.0
0.07079	0.1431	0.07806	0.1578	− 8.65
0.06701	0.1353	0.07389	0.1492	− 7.48
0.06066	0.1224	0.06690	0.1350	− 6.39
		G–*n*BuOH		
0.08995	0.1828	0.1434	0.2915	−24.7
0.08287	0.1684	0.1322	0.2686	−20.3
0.1041	0.2107	0.09528	0.1928	−19.0
0.07216	0.1463	0.1151	0.2333	−15.9

(Table 1. cont.)

		G–nBuOH		
0.09340	0.1888	0.08555	0.1728	−14.6
0.08701	0.1756	0.07963	0.1607	−12.5
0.07966	0.1610	0.07288	0.1473	−10.5
0.07167	0.1455	0.06557	0.1322	− 8.58
0.04075	0.08231	0.09774	0.1974	− 7.55
0.03762	0.7591	0.09020	0.1820	− 6.42

Table 2 Heats of dilution of ternary aqueous solutions of glycil-glycine (G_2) and alcohols at 25 °C

m_x^f	m_x^i	m_y^f	m_y^i	ΔH^{**}, J/kg
		G_2–nBuOH		
0.07329	0.1482	0.07171	0.1393	− 9.90
0.07059	0.1482	0.06635	0.1393	− 8.51
0.06893	0.1342	0.06477	0.1261	− 7.91
0.05714	0.1203	0.05372	0.1131	− 7.12
0.06377	0.1342	0.05992	0.1261	− 6.80
0.06114	0.1286	0.05743	0.1208	− 6.78
0.06182	0.1294	0.05809	0.1216	− 6.32
0.05714	0.1203	0.05372	0.1131	− 6.12
0.05707	0.1201	0.05360	0.1128	− 5.85
0.05134	0.1078	0.05391	0.1130	− 5.04
		G_2–tBuOH		
0.1145	0.2424	0.05900	0.1249	−16.8
0.1043	0.2202	0.05376	0.1135	−14.2
0.1102	0.2334	0.05682	0.1203	−13.4
0.07497	0.1455	0.08120	0.1576	−11.1
0.09083	0.19105	0.04681	0.09870	−10.4
0.07157	0.1388	0.07750	0.1503	−10.2
0.08770	0.1848	0.04519	0.09522	− 9.64
0.08417	0.1779	0.04337	0.09167	− 9.22
0.06399	0.1236	0.06931	0.1340	− 7.56
0.05754	0.1112	0.06235	0.1205	− 6.63
0.04894	0.09442	0.05303	0.1023	− 5.08
0.03770	0.07277	0.06889	0.1330	− 4.31
0.03480	0.06717	0.06358	0.1227	− 3.42
0.02987	0.05757	0.05458	0.1052	− 2.50
0.02927	0.05650	0.05352	0.1033	− 2.46
0.02609	0.05027	0.04769	0.09189	− 1.93
0.05454	0.1145	0.003652	0.007666	− 0.78
0.05969	0.1249	0.003998	0.008365	− 0.69
0.04751	0.09949	0.003181	0.006662	− 0.64

Table 3 Heats of dilution of ternary aqueous solutions of glycil-glycil-glycine (G_3) and alcohols at 25 °C

		G_3–*n*BuOH		
m_x^f	m_x^i	m_y^f	m_y^i	ΔH^{**}, J/kg
0.02437	0.004723	0.05959	0.1155	− 2.89
0.02297	0.04449	0.05618	0.1088	− 2.47
0.01326	0.03393	0.03979	0.08301	− 2.39
0.01958	0.04107	0.04792	0.1005	− 2.06
0.03042	0.06122	0.02969	0.05975	− 2.28
0.01885	0.03795	0.04918	0.09901	− 2.00
0.01811	0.03799	0.04432	0.09295	− 1.90
0.01582	0.03045	0.03947	0.7596	− 1.75
0.01505	0.02907	0.03754	0.07253	− 1.01
		G_3–*t*BUOH		
0.05059	0.1027	0.09700	0.1969	−15.5
0.04339	0.08793	0.08319	0.1686	−11.1
0.03725	0.07517	0.07144	0.1441	− 8.11
0.02857	0.05772	0.05480	0.1170	− 4.85
0.03616	0.07204	0.3712	0.07396	− 3.96
0.03360	0.06690	0.03450	0.06869	− 3.38
0.02323	0.04684	0.04454	0.08981	− 3.05
0.02652	0.05375	0.02722	0.05518	− 2.05
0.02153	0.04359	0.02210	0.04475	− 1.19
0.005348	0.01079	0.05492	0.01108	− 0.03

By means of a least squares method, the h_{xy} coefficients and their 95% confidence limits were determined for each of the six systems studied. In Tables 1–3 the initial and final molalities, and the values of the auxiliary function ΔH^{**}, are summarised for the four G-alcohol systems and for the two pairs of system containing *n*BuOH or *t*BuOH–G and G_2 or G_3, respectively.

Table 4 Pair enthalpic coeffiients h_{xy} between aminoacids and alcohols in water at 25 °C

y *x*	*G*	G_2	G_3	EtOH	*n*PrOH	*n*BuOH	*t*BuOH
G	−447 (—)[a]	—	—	553 (12)	654 (6)	799 (10)	914 (12)
G_2	—	−760 (7)[b]	—	—	—	877 (39)	1035 (42)
G_3			−1891 (52)[b]	—	—	1122 (132)	513 (13)
EtOH				243(10)	—	—	—
*n*PrOH					559 (14)[c]	—	—
*n*BuOH						1003 (15)[c]	—
*t*BuOH							656 (33)[c]

[a] Ref. [35]; [b] Ref. [40]; similar results are given in Refs [38] and [39]; [c] Ref. [8].

In Table 4 the values of the self and cross pair interaction coefficients for the systems studied are shown. All the cross coefficients are positive and two main points must be examined:

i) the strict similarity between the trend of the values of h_{xy} *vs.* those of the self coefficients of the alcohols for the systems containing glycine and the trends relative to the systems involving hydrophilic structure-breaking solutes, urea (U), thiourea (TU) and biuret (BU) and the four alcohols studied.

ii) The strict similarity of the trend of the value of h_{xy} *vs.* those of the self coefficients of G, G_2, G_3, for the systems containing *n*BuOH and *t*BuOH and the trends relative to the same two alcohols and U, TU, BU.

For all the trends a maximum in h_{xy} is found for the systems containing *t*BuOH. As reported in the literature [15], this maximum is an evidence of the self consistency of the proposed model of interaction, which postulates a prevailing release of water from the less stable, "ordered", cospheres of the hydrophobic structure-making solutes to the bulk, induced by the disruptive effect of the hydrophilic structure-breaking solutes (chaotropism). For *t*BuOH, the self pair interaction is less effective than for the linear isomer *n*BuOH, because of steric reasons. Then, a greater quantity of water molecules can be released from the cosphere of *t*BuOH, with respect to *n*BuOH, by the chaotropic effect of glycine and of any other hydrophilic structure-breaking solute studied. The h_{xy} values for glycine-alcohol systems are intermediate between those involving BU and TU and higher than those relative to U-alcohol systems. From this point of view, the chaotropic aptitude of glycine seems more effective than that of U or TU and less than that of BU. The inversion of the values of the cross coefficients for TU and G_2, as compared to the self ones, underlines that a supplementary effect is induced by the aminoacid, probably because of its zwitterionic nature that could be responsible for the extra release of water molecules from the cospheres of the alcohols. As a proof supporting this hypothesis it can be observed that the cross coefficients for the

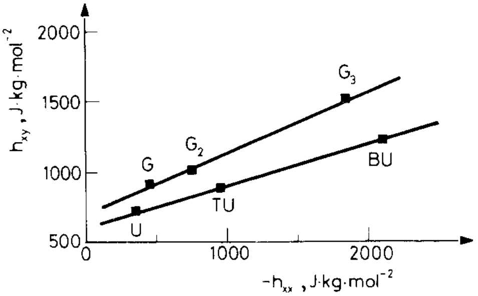

Fig. 1 Cross interaction coefficients for the systems containing *t*-butanol and G, G_2, G_3, U, TU, BU versus the self coefficients of the destructuring solute

interaction for G, G_2, G_3 and *n*BuOH or *t*BuOH are all higher than those for U, TU, BU (for *t*BuOH see Figure 1) underlining also in these cases the presence of an extra contribution to the chaotropic effect, probably due to the presence of the zwitterionic form. This effect cannot be taken into account on the basis of the knowledge of the values of the self interaction coefficients.

On the other hand, the behaviour of G, G_2, G_3 toward the alcohols is really similar to that of the other urea-like solutes, thus underlining the self consistency of the simple model proposed for the interaction of two opposite classes of solutes. Namely, a unique mechanism operates in all the cases quoted: the release of water from the labile cospheres of alcohols to the bulk. In the systems here cited this is the effect that largely overwhelms all the possible others, determining the sign and the values of the h_{xy} parameters.

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Zusammenfassung — Die Verdünnungsenthalpien ternärer wässeriger Lösungen, die einen Alkohol (Ethanol, *n*-Propanol, *n*-Butanol oder *tert*-Butanol) und eine Aminosäure oder ein Peptid (Glycin, Glycil-glycin oder Glycyl-glycyl-glycin) enthalten, wurden bei 25 °C gemessen. Die erhaltenen Werte wurden zur Berechnung der Parameter der zwischen den Molekülen der verschiedenartigen gelösten Stoffe auftretenden Wechselwirkungen herangezogen. Die Koeffizienten der Virialentwicklung der Überschussenthalpien werden mit denen verglichen, die sich auf die gleichen Alkohole und andere strukturbrechende gelöste Stoffe (Harnstoff, Thioharnstoff und Biuret) enthaltenden Lösungen beziehen. Die Enthalpieparameter der Systeme Glycin-Alkohole zeigen den in der Literatur für ähnliche strukturbrechende gelöste Stoffe mitgeteilten Trend nämlich ein Maximum in der Kurve, die beim Auftragen der Koeffizienten der Wechselwirkung zwischen verschiedenartigen Molekülen gegen die

Koeffizienten der Wechselwirkung zwischen den Alkoholmolekülen erhalten wird. Die Ergebnisse werden unter Annahme eines bevorzugten Austritts von Wasser aus der Kosphäre der Alkohole interpretiert.

Резюме — При 25° измерены энтальпии разбавления тройных водных систем, содержащих спирт (этанол, н-пропанол, н-бутанол или трет-бутанол), аминокислоту или пептид (глицин, глицилглицин или глицил-глицил-глицин). Полученные результаты были использованы для вычисления двух параметров перекрестного взаимодействия между растворенными веществами. Коэффициенты действительного расширения избыточной энтальпии сопоставлены с таковыми для растворов, содержащих аналогичные спирты, но другие растворенные вещества (мочевину, тиомочевину и биурет). Энтальпийная пара параметров для системы глицин — спирты показале максимум на графической зависимости в координатах перекрестные коэффициенты — собственные коэффициенты взаимодействия спиртов, аналогично приведенной в литературе для подобных структурно-нарушенных растворенных веществ. Результаты объяснены на основе превалирующего вытеснения воды из косферы спиртов.