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INTERACTIONS BETWEEN HYDROPHILIC AND HYDROPHOBIC STRUCTURE MAKER SOLUTES.
EXCESS ENTHALPIES OF TERNARY AQUEOUS SOLUTIONS OF D-GLUCOSE AND ALCOHOLS AT 25 °C

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The coefficients of the virial expansion of the excess enthalpies of ternary aqueous solutions containing D-glucose and an alcohol (ethanol, *n*-propanol, *n*-butanol and *tert*-butanol) were determined at 25 °C. The trend of the cross coefficients versus the self coefficients of the alcohols exhibits a maximum in accordance with the system containing *tert*-butanol. This behaviour is similar to that found for the interaction of the same alcohols with any other hydrophilic solute examined up to now. The results are interpreted in terms of a prevailing release of water from the structured cospheres of the alcohols.

The so-called "non bonding" interactions play an important and often determining role in many biochemical reactions and processes, and as such they are extensively investigated [1]. Among them, the hydrophobic interactions in aqueous solutions are, probably, the most thoroughly investigated [2].

Studies on the heterotactic interactions between alcohols and hydrophilic structure breaking solutes have been reported in preceding papers [3–5]: the results were interpreted as being due to a prevailing release of water molecules from the structured, more labile, cosphere of the alcohols to the bulk. The same effect is obtained as for the hydrophobic interaction: the reduction of the hydrophobic cospheres. Hence, these cross interactions enhance the hydrophobic effect.

Here we present a calorimetric study at 25° of the interactions in water between D-glucose and ethanol (EtOH), *n*-propanol (*n*PrOH), *n*-butanol (*n*BuOH) and *tert*-butanol (*t*BuOH).

Monosaccharides, already classified as hydrophilic structuring solutes, on the basis of the signs of the homotactic coefficients of the excess properties [6] and of spectroscopic evidences [7, 8], show a complex behaviour. In fact, when they interact with hydrophilic structure breaking solutes such as urea, thiourea and

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biuret, the negative sign and the invariance of the second enthalpic heterotactic coefficients must be noted. This suggests the presence in the hydration shells of the saccharide of distorted domains whose geometry is not compatible with the tetrahedral arrangement of water. On the basis of the small variability of the heterotactic coefficients, it can be assumed that the extension of these regions should be almost the same for all the monosaccharides.

The aim of this paper is just to go further into the investigation of monosaccharides and to see how they behave in the presence of typical hydrophobic solutes such as the alcohols.

Experimental

Materials and methods

D-Glucose (Sigma product) and ethanol (EtOH), *n*-propanol (*n*PrOH), *n*-butanol (*n*BuOH) and *tert*-butanol (*t*BuOH) (Carlo Erba products, spectroscopic grade) were used without further purification. Solutions were prepared by weight before each set of measurements. Water was deionized, twice distilled and filtered on a millipore membrane.

The heats of dilution of the ternary aqueous solutions, $\Delta_{\mathrm{dil}}H$ (J/kg of water in the final solution), determined by means of a LKB 10700–1 standard flow micro-calorimeter at 25 ± 0.02°, are given by:

$$\Delta_{\mathrm{dil}}H[(m_x^i, m_y^i) \rightarrow (m_x^f, m_y^f)] = -(\mathrm{d}Q/\mathrm{d}t)/P_w \qquad (1)$$

where $\mathrm{d}Q/\mathrm{d}t$ (watts) is the heat evolved per time unit in steady state conditions; P_w is the total mass flow rate of water, and m^i and m^f are the initial and final molalities, respectively. Other experimental details have been described in preceding papers [3, 9].

Results and discussion

The excess enthalpy of a ternary solution can be expressed as a virial expansion of the molalities as follows [10, 11]:

$$\Delta_{\mathrm{dil}}H^{\mathrm{E}}(m_x, m_y) = h_{xx}m_x^2 + 2h_{xy}m_xm_y + h_{yy}m_y^2 + \textit{higher terms} \qquad (2)$$

The h coefficients, on the basis of the McMillan–Mayer approach [12], represent the enthalpic contribution to the free energy coefficients: the last ones characterize the interactions among pairs, triplets and higher numbers of solute molecules of the same or different species. They account implicitly for the solute-solvent and solvent-solvent interactions.

The enthalpy of dilution of the ternary solution is related to the excess enthalpy, and finally to the cross coefficients through an auxiliary function ΔH^{**}, according to the following relations [13]:

$$\Delta_{\mathrm{dil}}H[(m_x^i, m_y^i)\rightarrow(m_x^f, m_y^f)] = H^E(m_x^f, m_y^f) - m_x^f/m_x^i H^E(m_x^i, m_y^i) \tag{3}$$

$$\begin{aligned}\Delta H^{**} &= \Delta_{\mathrm{dil}} H[(m_x^i, m_y^i)\rightarrow(m_x^f, m_y^f)] - \Delta_{\mathrm{dil}}H(m_x^i \rightarrow m_x^f) - \Delta_{\mathrm{dil}}H(m_y^i \rightarrow m_y^f) = \\ &= 2h_{xy}m_x^f m_y^f + \mathit{higher\ terms}\end{aligned} \tag{4}$$

For the substances here studied, the homotactic coefficients are known from the literature [13, 14], while the heterotactic coefficients of Eq. (4) are evaluated through a least squares method with their own 95% confidence limits. The concentration range explored was limited and then the calculation procedure requires only the determination of the pair heterotactic coefficients.

In Tables 1–4 the initial and final molalities are reported, along with the auxiliary function ΔH^{**} for the systems under examination. In Table 5 the homotactic and heterotactic interaction coefficients are shown: as can be seen, they are positive, very high in value, and increasing with increasing length of the alkyl chain. Hence, this interaction seems to be characterized by the release of water prevailingly from the hydrophobic cosphere of the alcohols. In Fig. 1 the heterotactic coefficients are plotted versus the number of carbon atoms, *n*C, for all the systems already described in the literature, including normal alcohols and hydrophilic structure breakers. The trends are almost linear. In Fig. 2 the heterotactic coefficients versus the homotactic ones of the branched and normal alcohols are shown. The system D-glucose/*t*BuOH is characterized by a cross coefficient higher than that relative to the normal alcohol.

Table 1 Heats of dilution of ternary aqueous solutions of D-glucose and ethanol at 25 °C

m_x^i	m_x^f	m_y^i	m_y^f	ΔH^{**}, J/kg
0.4851	0.2217	0.4065	0.1858	−72.7
0.4078	0.1874	0.3417	0.1570	−51.9
0.3589	0.1658	0.3417	0.1570	−40.6
0.3475	0.1606	0.2912	0.1346	−38.6
0.3374	0.1561	0.2827	0.1308	−35.8
0.3236	0.1500	0.2711	0.1256	−33.3
0.2217	0.1035	0.1858	0.08678	−15.4
0.1874	0.08778	0.1570	0.07354	−10.6
0.1561	0.07372	0.1308	0.06139	− 7.08
0.08778	0.04142	0.07354	0.03470	− 2.28

Table 2 Heats of dilution of aqueous solutions of D-glucose and *n*-propanol at 25 °C

m_x^i	m_x^f	m_y^i	m_y^f	ΔH^{**}, J/kg
0.4098	0.2031	0.3701	0.1834	−70.1
0.3669	0.1824	0.3314	0.1648	−56.5
0.3359	0.1673	0.3034	0.1512	−47.3
0.2157	0.1069	0.4553	0.2257	−46.9
0.2725	0.1365	0.2461	0.1232	−32.0
0.1638	0.08190	0.3457	0.1729	−26.6
0.2382	0.1196	0.2151	0.1080	−23.9
0.1454	0.07290	0.3069	0.1539	−21.3
0.1183	0.05950	0.2496	0.1256	−14.1

Table 3 Heats of dilution of aqueous solutions of D-glucose and *tert*-butanol at 25 °C

m_x^i	$m_x^{f'}$	m_y^i	m_y^f	ΔH^{**}, J/kg
0.4227	0.2071	0.4934	0.2417	−126.5
0.3415	0.1688	0.3986	0.1970	− 81.6
0.2839	0.1414	0.3314	0.1651	− 56.0
0.1984	0.09850	0.4059	0.2015	− 49.4
0.2367	0.1185	0.2763	0.1384	− 39.2
0.2052	0.1030	0.2395	0.1202	− 29.6
0.1512	0.07570	0.3094	0.1549	− 28.2
0.1749	0.08810	0.2042	0.1028	− 21.3
0.1263	0.06350	0.2584	0.1300	− 20.0

Table 4 Heats of dilution of aqueous solutions of D-glucose and *n*-butanol at 25 °C

m_x^i	m_x^f	m_y^i	m_y^f	ΔH^{**}, J/kg
0.3173	0.1577	0.3404	0.1692	−57.6
0.2763	0.1380	0.2964	0.1481	−44.0
0.1765	0.08786	0.4457	0.2219	−43.0
0.2363	0.1182	0.2535	0.1268	−33.5
0.2328	0.1167	0.2498	0.1252	−31.6
0.1469	0.07355	0.3709	0.1857	−29.3
0.1960	0.09860	0.2103	0.1058	−22.9
0.1279	0.06427	0.3230	0.1623	−22.3
0.1127	0.05621	0.2846	0.1419	−18.2

Table 5 Enthalpic pairwise interaction coefficients for D-glucose and alkanols at 25 °C

x	y	h_{xx}	h_{yy}	h_{xy}
			J mol/kg	
EtOH	D-glucose	243 (10)	343 (10)	750 (6)
n-PrOH	D-glucose	559 (14)	— „ —	934 (9)
n-BuOH	D-glucose	1003 (15)	— „ —	1083 (13)
tert-BuOH	D-glucose	656	— „ —	1208 (7)

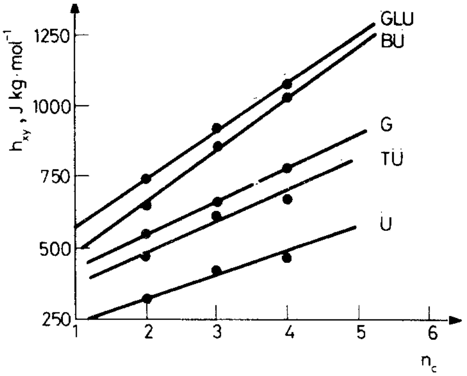

Fig. 1 Heterotactic coefficients *vs.* the number of carbon atoms, n_c, for linear alkanols

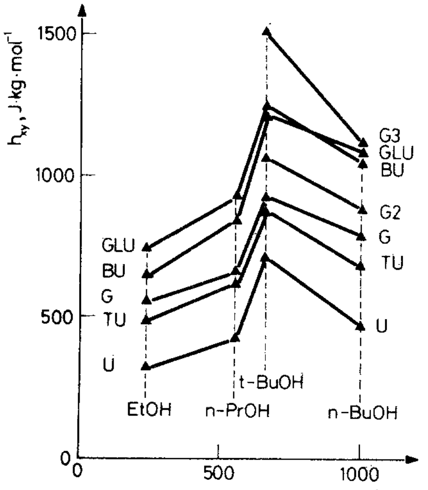

Fig. 2 Heteroactic coefficients *vs.* the homotactic ones for branched and normal alkanols

This behaviour has already received an explanation [3], relying on the preservation of the hydrophobic hydration cosphere of the branched alcohol compared to the linear ones, occurring upon the self interaction. The minor juxtaposition of the alkyl chains of the branched alcohol leads to a minor release of water in the overlap of the cospheres: hence the action of a solute, which makes the hydrophobic cospheres to collapse, is more effective.

As clearly shown in Fig. 2, the h_{xy} coefficients, beyond their positive sign, are the highest in value among those characterizing the interaction of alcohols with hydrophilic structure breakers. Namely, D-glucose appears to behave not differently from these destructuring substances: it is even more powerful than biuret. As already mentioned, saccharides are solutes whose behaviour in water has been characterized as that of hydrophilic structure makers [6]. However, there are evidences that their behaviour has a more complex nature. In fact, they resemble rather the destructuring solutes upon interaction with urea-like solutes [3–5]. The presence of furanose forms, the ring oxygen, the —OH axial groups, the mutarotation process and other conformational transitions have been invoked as sources of perturbation of the ordered hydration cage, induced and stabilized by chair conformers showing the maximum number of equatorial —OH [15, 16]. However, the interaction with alcohols seems to be simply characterized by the release of water prevailingly from the more labile hydrophobic cosphere of the alcohols. The interaction between these two classes of solutes is, once again, explained through a mechanism not differing from the other one proposed for urea-alkanol interaction in water: a competition for water between hydrophilic and hydrophobic solutes. The more labile hydration cosphere of the hydrophobic solutes is partially destroyed in this interaction. The same mechanism operates also in the case of the interaction of the same alcohols with glycine and its oligomers [15]. In this case, however, there is a supplementary effect induced by the aminoacid, whose zwitterionic nature is probably responsible for an extra release of water from the cospheres of the alcohols. Hence the aptitude to subtract free water (for building up their own hydration spheres) makes the aminoacids more effective than urea and thiourea in promoting the transfer of water from the hydration shells of the hydrophobic solutes to the bulk. This is clearly shown by the similarity among the trends shown in the Figures. This paper, we think, gives further proofs of the multiform behaviour of monosaccharides: different perturbations make them to respond differently and they can behave in turn as hydrophilic structure makers, or as hydrophilic structure breakers in the presence of urea-like solutes or prevailingly hydrophobic solutes.

Moreover, there are evidences that they behave as hydrophobic solutes in the presence of extended hydrophobic surfaces [17].

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Zusammenfassung — Die Koeffizienten der Virialentwicklung der Überschußenthalpien von ternären, D-Glucose und einen Alkohol (Ethanol, *n*-Propanol, *n*-Butanol, *tert*-Butanol) enthaltenden wässrigen Lösungen wurden bei 25 °C bestimmt. Bei dem tert-Butanol enthaltenden System wird ein Maximum erhalten, wenn die Koeffizienten der Wechselwirkung zwischen verschiedenartigen Molekülen gegen die Wechselwirkung zwischen den Alkoholmolekülen aufgetragen werden. Dieses Verhalten ist identisch mit dem, das für die Wechselwirkung der gleichen Alkohole mit anderen bis jetzt untersuchten hydrophilen gelösten Stoffen gefunden wurde. Die Ergebnisse werden interpretiert, indem ein bevorzugter Austritt von Wasser aus der strukturierten Koordinationssphäre des Alkohols angenommen wird.

Резюме — При 25° определены коэффициенты действительного расширения избыточной энтальпии тройных водных систем, содержащих Д-глюкозу и спирт (этанол, н-пропанол, н-бутанол или трет-бутанол). Зависимость перекрестных коэффициентов от собственных коэффициентов спиртов показывает максимум для системы с третичным бутанолом. Такая тенденция является общей для всех случаев взаимодействия аналогичных спиртов с каким-либо другим гидрофильным растворенным веществом. Полученные результаты обсуждены на основе преобладающего вытеснения воды из структурных косфер спиртов.