J Solution Chem (2011) 40: 93–105
DOI 10.1007/s10953-010-9627-5

Intermolecular Interactions in Ternary Glycerol–Sample–H_2O: Towards Understanding the Hofmeister Series (V)

Peter Westh · Erik Lumby Rasmussen · Yoshikata Koga

Received: 6 February 2010 / Accepted: 7 July 2010 / Published online: 30 November 2010

Abstract We studied the intermolecular interactions in ternary glycerol (Gly)–sample (S)–H_2O systems at 25 °C. By measuring the excess partial molar enthalpy of Gly, $H^{\mathrm{E}}_{\mathrm{Gly}}$, we evaluated the Gly–Gly enthalpic interaction, $H^{\mathrm{E}}_{\mathrm{Gly–Gly}}$, in the presence of various samples (S). For S, tert-butanol (TBA), 1-propanol (1P), urea (UR), NaF, NaCl, NaBr, NaI, and NaSCN were used. It was found that hydrophobes (TBA and 1P) reduce the values of $H^{\mathrm{E}}_{\mathrm{Gly–Gly}}$ considerably, but a hydrophile (UR) had very little effect on $H^{\mathrm{E}}_{\mathrm{Gly–Gly}}$. The results with Na salts indicated that there have very little effect on $H^{\mathrm{E}}_{\mathrm{Gly–Gly}}$. This contrasts with our earlier studies on 1P–S–H_2O in that Na^+, F^- and Cl^- are found as hydration centers from the induced changes on $H^{\mathrm{E}}_{\mathrm{IP–IP}}$ in the presence of S, while Br^-, I^-, and SCN^- are found to act as hydrophiles. In comparison with the Hofmeister ranking of these ions, the kosmotropes are hydration centers and the more kosmotropic the higher the hydration number, consistent with the original Hofmeister's concept of "H_2O withdrawing power." Br^-, I^- and SCN^-, on the other hand, acted as hydrophiles and the more chaotropic they are the more hydrophilic. These observations hint that whatever effect each individual ion has on H_2O, it is sensitive only to hydrophobes (such as 1P) but not to hydrophiles (such as Gly). This may have an important bearing towards understanding the Hofmeister series, since biopolymers are amphiphilic and their surfaces are covered by hydrophobic as well as hydrophilic parts.

Keywords Effect of solute on H_2O · Ternary systems · Glycerol(Gly)–sample–H_2O · Gly–Gly interactions · Reduction of Gly–Gly interaction by hydrophobes · No effects on Gly–Gly interaction by hydrophiles and hydration centers · Gly-probing methodology

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Electronic supplementary material The online version of this article (doi:10.1007/s10953-010-9627-5) contains supplementary material, which is available to authorized users.

P. Westh · E.L. Rasmussen
NSM Research Unit for Functional Biomaterials, Roskilde University, Roskilde 4000, Denmark

Y. Koga (✉)
Department of Chemistry, The University of British Columbia, Vancouver, BC, Canada V6T 1Z1
e-mail: koga@chem.ubc.ca

1 Introduction

We have introduced a differential approach in solution thermodynamics and applied it to aqueous solutions with some success in gaining deeper insights into the molecular processes, what we call mixing schemes, in aqueous solutions [1–3]. Without using any model, we determine what we call the solute (i)–solute (j) enthalpic interaction, H^{E}_{i-j} defined as:

$$H^{\mathrm{E}}_{i-j} \equiv N\left(\frac{\partial H^{\mathrm{E}}_i}{\partial n_j}\right) = (1 - x_j)\left(\frac{\partial H^{\mathrm{E}}_i}{\partial x_j}\right) - \Sigma' x_k\left(\frac{\partial H^{\mathrm{E}}_i}{\partial x_i}\right) \tag{1}$$

Σ' of the second term on the far right signifies the sum for k from 1 to $m - 1$ except for i for an m-component system. The second equality is for the mole fraction variable system $(x_i\ (i = 1, 2, \ldots, (m - 1)), N)$ for convenience of experimentalists. n_i is the molar amount of the i-th component $(i = 1, 2, 3, \ldots, m)$. Note that the second term vanishes for a binary system. H^{E}_i is the excess partial molar enthalpy of i, and is defined as:

$$H^{\mathrm{E}}_i = \left(\frac{\partial H^{\mathrm{E}}}{\partial n_i}\right), \tag{2}$$

where H^{E} is the excess enthalpy of the entire system. The partial derivatives for the above and subsequent equations are taken keeping all the variables constant except that of the differentiation. Equation (2) indicates that H^{E}_i is the effect of an infinitesimal increase in n_i on the excess enthalpy of the entire system H^{E}. Thus, H^{E}_i signifies the actual contribution of the i-th component to H^{E}, or the actual enthalpic situation of i within the complex mixture. Hence, Eq. 1 suggests that H^{E}_{i-j} is the response of the system in terms of H^{E}_i, the actual enthalpic situation of i, when perturbed by an infinitesimal increase in n_j. We call it therefore the i–j enthalpic interaction [2–4].

Here we apply the same methodology on ternary glycerol (Gly)–sample(S)–H_2O systems, in order to see the effects of S on $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$. First, however, we revisit binary the Gly–H_2O system to confirm our earlier conclusions. Our earlier studies on binary Gly–H_2O indicated [5, 6] that it belongs to the class of hydrophilic solutes together with urea (UR) [7, 8] and others [5–9]. Based on these studies, we suggested that in the H_2O-rich region a hydrophile forms hydrogen bonds directly to the existing network of H_2O and keeps the connectivity of the hydrogen bond network of H_2O intact. However, its presence in the network retards the degree of fluctuation enjoyed in pure H_2O by breaking a local H donor/acceptor symmetry. In this composition region, H_2O retains its integrity in that the hydrogen bond network of H_2O is still bond-percolated [2–4]. The existence of the bond-percolated hydrogen bond network is also true in the H_2O-rich region in the presence of a hydrophobic solute [2–4, 10]. As the hydrophile's mole fraction increases to about 0.1, however, the availability of H_2O is too limited for keeping the network intact, and an additional solute starts to cluster together and what we call Mixing Scheme II sets in, where the solution consists of two kinds of clusters, one rich in H_2O and the other in solute molecules. However, our earlier studies of binary Gly–H_2O [5] and ternary 1P–Gly–H_2O [11] systems contain minor shortcomings, which will be fixed below as we first revisit the calorimetric works of both systems. As will become evident, the new data confirm the general conclusions regarding the effect of a hydrophile on H_2O discussed above. We then study the ternary Gly–S–H_2O systems, for S = tert-butanol (TBA), 1P, and urea (UR), and assess the effect of S on $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$. We then use NaF, NaCl, NaBr, NaI, and NaSCN for S, and study their effects on H_2O as seen by the induced changes, if any, on $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$. This is a part of our continuing efforts towards understanding the Hofmeister series [12–15].

2 Experimental

2.1 Chemicals Used

tert-Butanol (>99.3%, Sigma), 1-propanol (>99.8%, Fluka, and ACROS), urea (>99.5%, Merck), NaF (>99%, Sigma), NaCl (>99.5%, Merck), NaBr (>98%, BDH), NaI (>99.5%, Merck), and NaSCN$\cdot H_2O$ (>98%, Fluka) were used as supplied. Stock solutions were made gravimetrically using MiliQ H_2O and a sample from a freshly opened bottle. The titrand solution in the cell was prepared gravimetrically by diluting the stock solution immediately before measurements. Glycerol (>99.5%, Merck) for studies of binary and ternary systems was used as supplied with due care to avoid contamination by moisture.

2.1.1 Analysis of H_2O Content in Glycerol

The water content in the glycerol bottle in use was monitored regularly by a Karl Fischer Titrator (DL31, Metler-Toledo). We found water contents of 0.2–0.3% in freshly opened bottles. When a detectable increase in the water content could be established over the experimental noise (∼0.1%), the bottle was discarded.

2.2 Isothermal Titration Calorimetry

The excess partial molar enthalpy of Gly, $H^{\mathrm{E}}_{\mathrm{Gly}}$, was determined in a TAM 2277 thermal monitor equipped with type 2250, 1 mL micro reaction calorimeters (Thermometric). The reference was a 1 mL metal ampoule containing water. For direct determination of $H^{\mathrm{E}}_{\mathrm{Gly}}$, the partial derivative in the right of Eq. 2 was approximated by a quotient ($\delta H^{\mathrm{E}}/\delta n_{\mathrm{Gly}}$) with the amount of titrant $\delta n_{\mathrm{Gly}} \approx 10^{-7}$ mol. The titrand in the cell is about $N \approx 10^{-2}$ mol. This ratio of the titrant to the titrand is well within the acceptable range for the above approximation [16, 17]. In a previous work [5] glycerol was found to be too viscous to be readily delivered by the instrument manufacturer's syringes (needle inner diameter ∼100 μm). Hence, we mounted PEEK tubing with an inner diameter of 255 μm (Upchurch Scientific) on 500 μL glass syringes with Luer locks fittings (SGE) to facilitate the delivery. The home-made syringes were operated in Lund 2 pumps (Thermometric) and this improved the reproducibility of the results considerably from the previous work [5], and the uncertainties in $H^{\mathrm{E}}_{\mathrm{Gly}}$ are estimated as $\pm 20\ \mathrm{J\cdot mol^{-1}}$.

The excess partial molar enthalpy of 1P, $H^{\mathrm{E}}_{\mathrm{1P}}$, for the 1P–Gly–$H_2O$ system was determined by a home-made titration calorimeter of similar design to LKB Bromma [16]. Briefly, about 5 mol (N) of S–H_2O solution at a desired x^0_S (S = Gly) was measured in a titration cell, into which about 10 mmol of 1P (δn_{1P}) was titrated successively. The thermal response δH^{E} was determined, and the partial derivative of the right of Eq. 2 was approximated with the quotient $\delta H^{\mathrm{E}}/\delta n_{\mathrm{1P}}$. This ratio of the titrant to the titrand ($\delta n_{\mathrm{1P}}/N$) is also acceptable [16, 17].

3 Results and Discussion

Figure 1(a) shows five series of the measured values of $H^{\mathrm{E}}_{\mathrm{Gly}}$ for binary Gly–H_2O together with our earlier data [5]. It is clear that the reproducibility of $H^{\mathrm{E}}_{\mathrm{Gly}}$ is improved considerably. We now evaluate $H^{\mathrm{E}}_{\mathrm{Gly\text{–}Gly}}$, Eq. 1, with $i = j =$ Gly graphically without resorting to any fitting function. We draw a smooth curve through all the data points with aid of a flexible

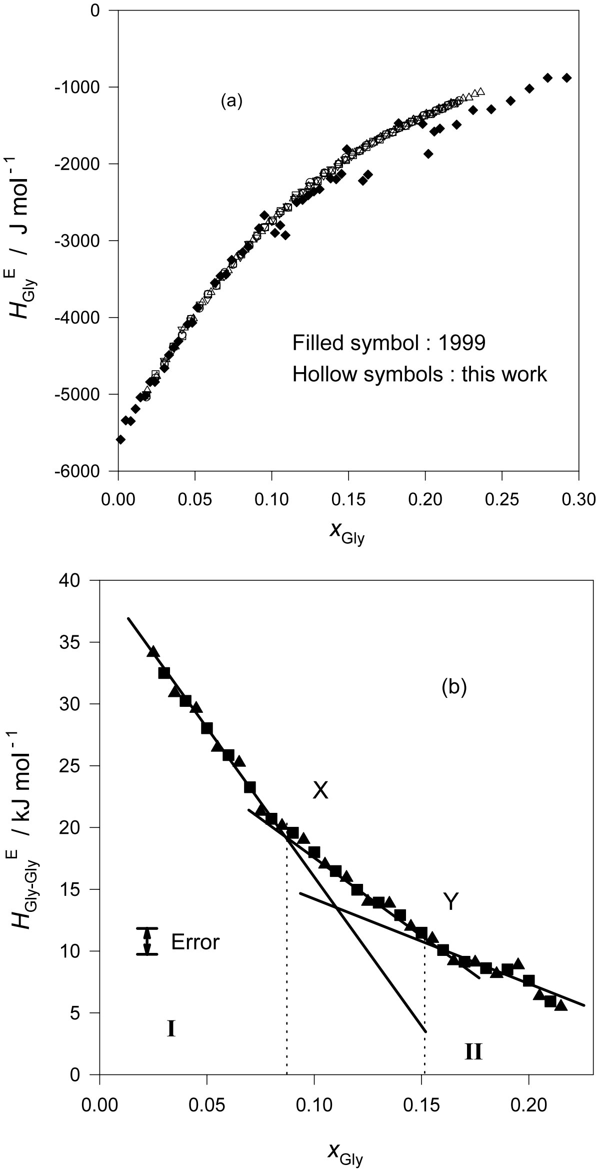


Fig. 1 (**a**) The excess partial molar enthalpy of glycerol (Gly), $H_{\text{Gly}}^{\text{E}}$, for binary Gly–$H_2O$ at 25 °C. *Filled diamonds* are our earlier data, which suffers from difficulty in smooth delivery of viscous Gly [5]. (**b**) The Gly–Gly enthalpic interaction, $H_{\text{Gly–Gly}}^{\text{E}}$, for binary Gly–$H_2O$ at 25 °C. The uncertainty is estimated as $\pm 1\ \text{kJ}\cdot\text{mol}^{-1}$. **I** and **II** indicates the regions of Mixing Scheme I and II. Point X marks the onset and Y the end point of the transition from Mixing Scheme I to II. *Triangle symbols* are for graphical differentiation with the increment $\delta x_{\text{Gly}} = 0.01$ and *squares* with $\delta x_{\text{Gly}} = 0.02$

ruler. We read the value of $H_{\text{Gly}}^{\text{E}}$ off the smooth curve drawn at the interval of $\delta x_{\text{Gly}} = 0.01$. We then approximate the partial derivative in Eq. 2 with the quotient, $(\delta H_{\text{Gly}}^{\text{E}}/\delta x_{\text{Gly}})$, with $\delta x_{\text{Gly}} = 0.01$ and 0.02. The results are shown in Fig. 1(b). The uncertainty in $H_{\text{Gly–Gly}}^{\text{E}}$ in this binary system was estimated as $\pm 1\ \text{kJ}\cdot\text{mol}^{-1}$. As evident in the figure, both plots with $\delta x_{\text{Gly}} = 0.01$ and 0.02 lie on the same three sets of straight lines. This validates the above approximation, and more importantly, the x_{Gly}-dependence pattern of $H_{\text{Gly–Gly}}^{\text{E}}$ shows indeed the hallmark of a hydrophile [6, 18]. Thus, up to point X_{Gly} for Gly–H_2O in the figure, $x_{\text{Gly}} = 0.09$, the hydrogen bond network of H_2O is still bond percolated [6, 18]. In the

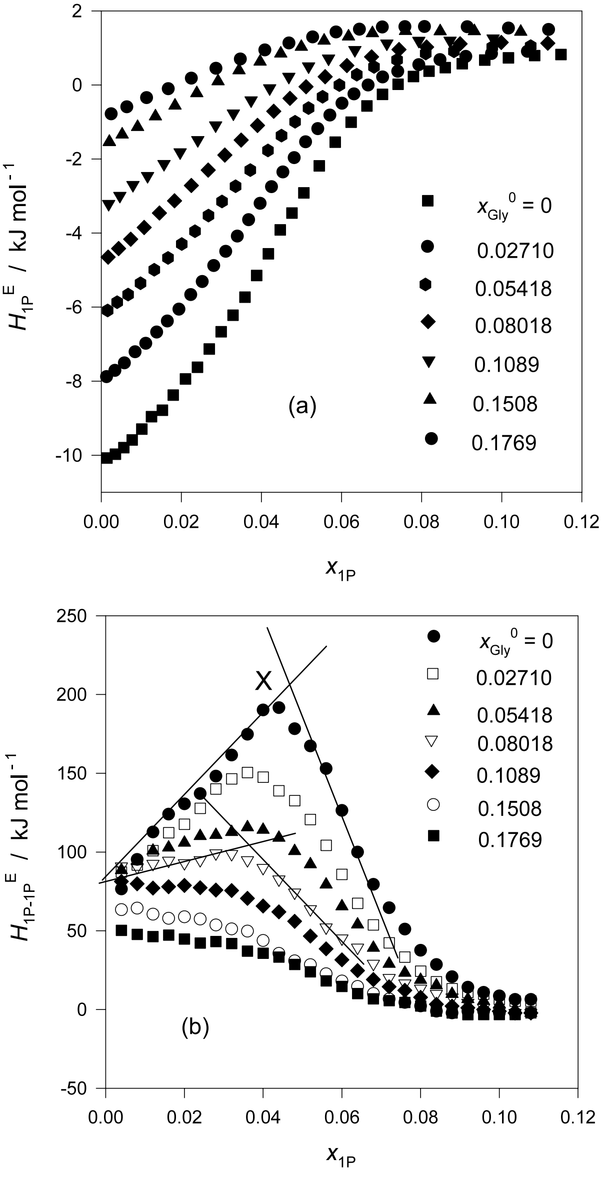


Fig. 2 (**a**) The excess partial molar enthalpy of 1P, H_{1P}^{E}, in 1P–Gly–H_2O at 25 °C. x_{Gly}^{o} is the initial mole fraction of Gly prior to 1P titration. (**b**) The 1P–1P enthalpic interaction, H_{1P-1P}^{E}, in 1P–Gly–H_2O at 25 °C. The uncertainty is about ±10 kJ·mol^{-1}

range $0.09 < x_{Gly} < 0.15$ the transition from Mixing Scheme I to II proceeds and beyond 0.15 Mixing Scheme II is operative. Thus point Y_{Gly} is at $x_{Gly} = 0.15$. These findings about binary Gly–H_2O almost completely corroborate the recent conclusions drawn by a combined molecular dynamic simulation—IR study [19].

We now revisit the 1-propanol(1P)–Gly–H_2O ternary system to see if there are some new findings in the induced changes of the H_{1P-1P}^{E} pattern at the loci of point X_{Gly} and Y_{Gly}, $x_{Gly}^{o} = 0.09$ and 0.15. In our earlier work [11], we covered only up to $x_{Gly}^{o} = 0.1$, rather close to the boundary at $x_{Gly}^{o} = 0.09$. Figure 2(a) shows the H_{1P}^{E} data and Fig. 2(b) the resulting $H^{\mathrm{E}}_{\mathrm{1P-1P}}$. It is clear from Fig. 2(b) that the $H^{\mathrm{E}}_{\mathrm{1P-1P}}$ pattern is of a peak-type up to $x^{\mathrm{o}}_{\mathrm{Gly}} = 0.08$, but at 0.11 no initial increase is observed. This observation indicates that up to at least $x^{\mathrm{o}}_{\mathrm{Gly}} = 0.08$ the integrity of H_2O is retained, as discussed extensively earlier [20–22]. For $x^{\mathrm{o}}_{\mathrm{Gly}} > 0.11$, the $H^{\mathrm{E}}_{\mathrm{1P-1P}}$ pattern has some similarity in that there is a break in the slope, without an initial increase. This is consistent with the fact that in the range $0.09 < x^{\mathrm{o}}_{\mathrm{Gly}} < 0.15$, the process of hydrogen bond percolation being lost is in progress bit by bit from stronger hydrogen bonds to weaker ones [20–22]. However, whether there is a qualitative change between $x^{\mathrm{o}}_{\mathrm{Gly}} = 0.15$ and 0.17 for Y_{Gly} in Gly–H_2O is not clear. After all, point Y_{Gly} in Fig. 1(b) is rather obscure, being the intercept of the two lines with a smaller slope difference than that for point X_{Gly}. Finally, X_{Gly} for hydrophiles is much less clear, in terms of shape and value, than the $H^{\mathrm{E}}_{\mathrm{1P-1P}}$ counterpart, as is evident in Fig. 1(b), $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$, and Fig. 2(b), $H^{\mathrm{E}}_{\mathrm{1P-1P}}$. Thus an attempt at observing any induced changes in the $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$ patterns on addition of the test sample S would be rather challenging.

3.1 Effects of Tert-Butanol, 1-Propanol and Urea

We nevertheless seek the effect of the presence of S on the x_{Gly}-dependence pattern of $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$. Figure 3 shows the $x^{\mathrm{o}}_{\mathrm{Gly}}$ values in the ternary Gly–S–H_2O systems for given initial mole fractions of S, x^{o}_{S}. For S, tert-butanol (TBA), 1-propanol (1P), and urea (UR) are chosen. From previous studies, UR is a typical hydrophile [6–8]. TBA and 1P are known to be hydrophobes and that TBA is stronger than 1P [2–4]. In the H_2O-rich region, a hydrophobe enhances the hydrogen bond probability in its immediate vicinity similar to the classical picture of "iceberg formation", but more importantly the hydrogen bond probability of bulk H_2O away from iceberg-clad solutes is reduced progressively. When the mole fraction of the solute reaches the threshold value, dependent on its hydrophobicity, the bulk H_2O loses its bond-percolation character, and Mixing Scheme II, as for a hydrophile, sets in [2–4]. Since the bulk H_2O in the H_2O-rich region prior to the transition to Mixing Scheme II retains the hydrogen bond network, we also call this mixing scheme for hydrophobe Mixing Scheme I.

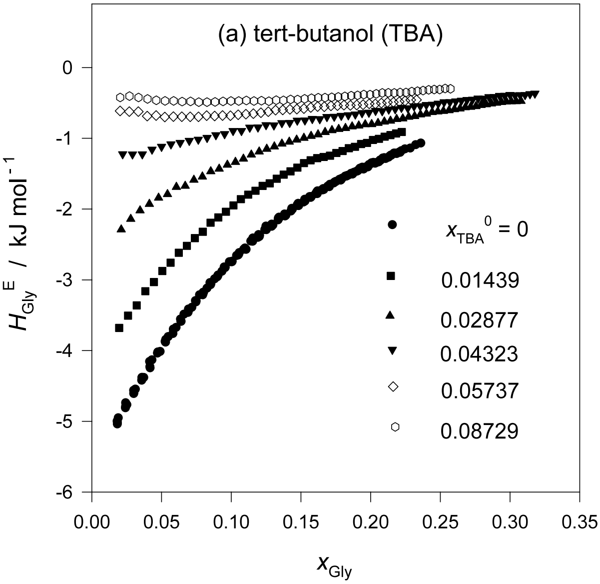


Fig. 3 (**a**) The excess partial molar enthalpy of Gly, $H^{\mathrm{E}}_{\mathrm{Gly}}$, in Gly–TBA–$H_2O$ at 25 °C. *Hollow symbols* indicate that the starting TBA–H_2O is in Mixing Scheme II region. (**b**) $H^{\mathrm{E}}_{\mathrm{Gly}}$ in Gly–1P–H_2O at 25 °C. *Hollow symbols* indicate that the starting 1P–H_2O is already in Mixing Scheme II region. (**c**) $H^{\mathrm{E}}_{\mathrm{Gly}}$ in Gly–1P–H_2O at 25 °C. *Hollow symbols* indicate that the starting 1P–H_2O is already in Mixing Scheme II region

Fig. 3 (*Continued*)

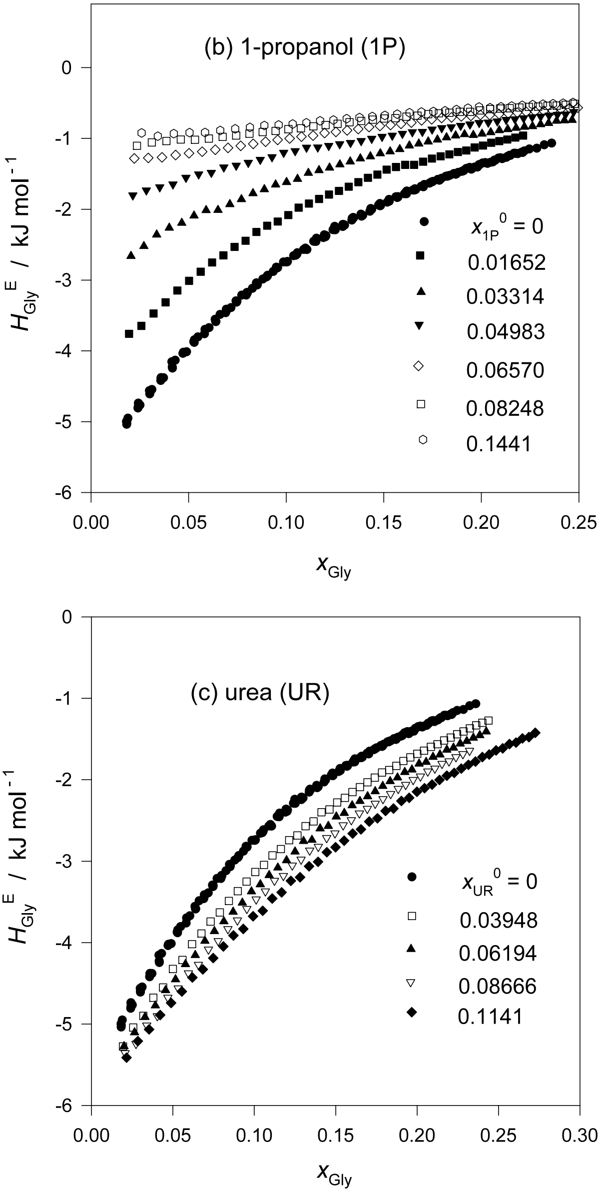


Figure 3(a) and (b) indicate that hydrophobes, TBA and 1P, increase the values of $H^{\mathrm{E}}_{\mathrm{Gly}}$ but reduce the modest positive x_{Gly}-dependence of $H^{\mathrm{E}}_{\mathrm{Gly}}$ as x^{o}_{S} (S = TBA or 1P) increases up to the Mixing Scheme boundaries, point X_{TBA} and $X_{\mathrm{1P}}x^{\mathrm{o}}_{\mathrm{TBA}} = 0.045$ and $x^{\mathrm{o}}_{\mathrm{1P}} = 0.05$, respectively [2–4]. We here limit our attention to within Mixing Scheme I where the integrity of H_2O is retained. A hydrophile, UR (Fig. 3(c)), on the other hand, reduces the values as well as the x_{Gly}-dependence of $H^{\mathrm{E}}_{\mathrm{Gly}}$. For UR, the integrity of H_2O was found to be retained up to x^{o}_{S} (S = UR) = 0.2 from our earlier works [7, 8].

To see these behaviors more clearly, we evaluate the third derivative quantities, $H^E_{\mathrm{Gly-Gly}}$. We draw a smooth curve through all the data points in Fig. 3 and read the value of H^E_{Gly} off the smooth curve drawn at the interval $\delta x_{\mathrm{Gly}} = 0.01$. We then calculate the Gly–Gly enthalpic interactions in Gly–S–H_2O by the right of Eq. 1 with $i = j = \mathrm{Gly}$. As for the binary Gly–H_2O discussed above, the value for $(\partial H^E_{\mathrm{Gly}}/\partial x_{\mathrm{Gly}})$ is approximated by $(\delta H^E_{\mathrm{Gly}}/\delta x_{\mathrm{Gly}})$ with $\delta x_{\mathrm{Gly}} = 0.02$. The uncertainty in $H^E_{\mathrm{Gly-Gly}}$ for ternary systems is estimated as $\pm 3\ \mathrm{kJ\cdot mol^{-1}}$, larger than that for the binary system in which there were five-fold more data points. Figure 4 shows the results for $H^E_{\mathrm{Gly-Gly}}$. The $H^E_{\mathrm{Gly-Gly}}$ pattern for the binary system seems generally retained on addition of S, although the locus of point X becomes more difficult to identify. The hydrophobes, TBA and 1P in Fig. 4(a) and (b) show general reduction in the values of $H^E_{\mathrm{Gly-Gly}}$ as well as the slopes in the figures as x^{o}_S increases. A hydrophilic UR, Fig. 4(c), on the other hand, reduces $H^E_{\mathrm{Gly-Gly}}$ very little. As $x^{\mathrm{o}}_{\mathrm{UR}}$ increases, the slopes are also reduced and the location of point X_{Gly} becomes obscure. Whether point X_{Gly} shifts to a smaller value of x_{Gly}, which would be expected if the H_2O molecules in the hydration shell be made unavailable for Gly to interact, is not clear.

In order to quantify the above effects by an individual sample, it would be convenient if the loci of point X_{Gly} be followed as a function of x^{o}_S. However, the loci of point X_{Gly} are obscure for the most of the present cases. Therefore we instead use the value of $H^E_{\mathrm{Gly-Gly}}$ extrapolated linearly to $x_{\mathrm{Gly}} = 0$ and that at the fixed mole fraction $x_{\mathrm{Gly}} = 0.1$ and follow their x^{o}_S-dependences. The point at $x_{\mathrm{Gly}} = 0.1$ is presumably near but past X_{Gly} for general Gly–S–H_2O. Figure 5 shows $H^E_{\mathrm{Gly-Gly}}$ as a function of x^{o}_S. At $x_{\mathrm{Gly}} = 0$, Fig. 5(a), $H^E_{\mathrm{Gly-Gly}}$ diminishes rapidly for hydrophobic TBA and 1P up to the Mixing Scheme boundaries point X_{TBA} and X_{1P}, shown by the dotted line in the figure. This is due to the reduction of the hydrogen bond probability of bulk H_2O away from iceberg-clad hydrophobes. Thus, the Gly–Gly interaction, occurring via the hydrogen bond network of bulk H_2O, becomes smaller in H_2O with progressively lower hydrogen bond probability. Hydrophilic UR also diminishes $H^E_{\mathrm{Gly-Gly}}$ but to a much lesser degree. This may be related to the fact that an inter-hydrophilic interaction $H^E_{\mathrm{Gly-Gly}}$ itself is much smaller than that for a hydrophobic counterpart. In the

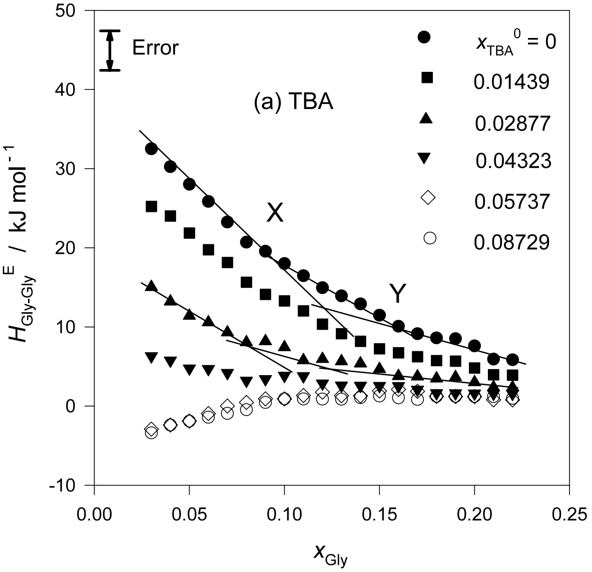
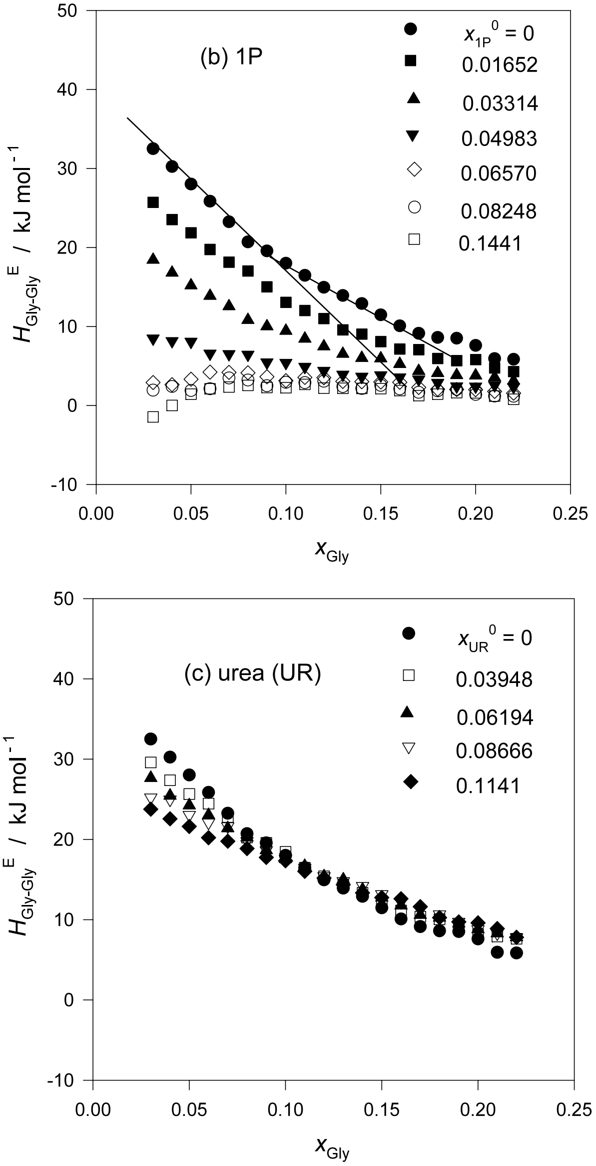


Fig. 4 (**a**) $H^E_{\mathrm{Gly-Gly}}$ in Gly–TBA–H_2O at 25 °C. *Hollow symbols* indicate that the starting TBA–H_2O is already in Mixing Scheme II. The uncertainty is estimated as $\pm 3\ \mathrm{kJ\cdot mol^{-1}}$. (**b**) $H^E_{\mathrm{Gly-Gly}}$ in Gly–1P–H_2O at 25 °C. *Hollow symbols* indicate that the starting 1P–H_2O is already in Mixing Scheme II. (**c**) $H^E_{\mathrm{Gly-Gly}}$ in Gly–UR–H_2O at 25 °C

Fig. 4 (*Continued*)

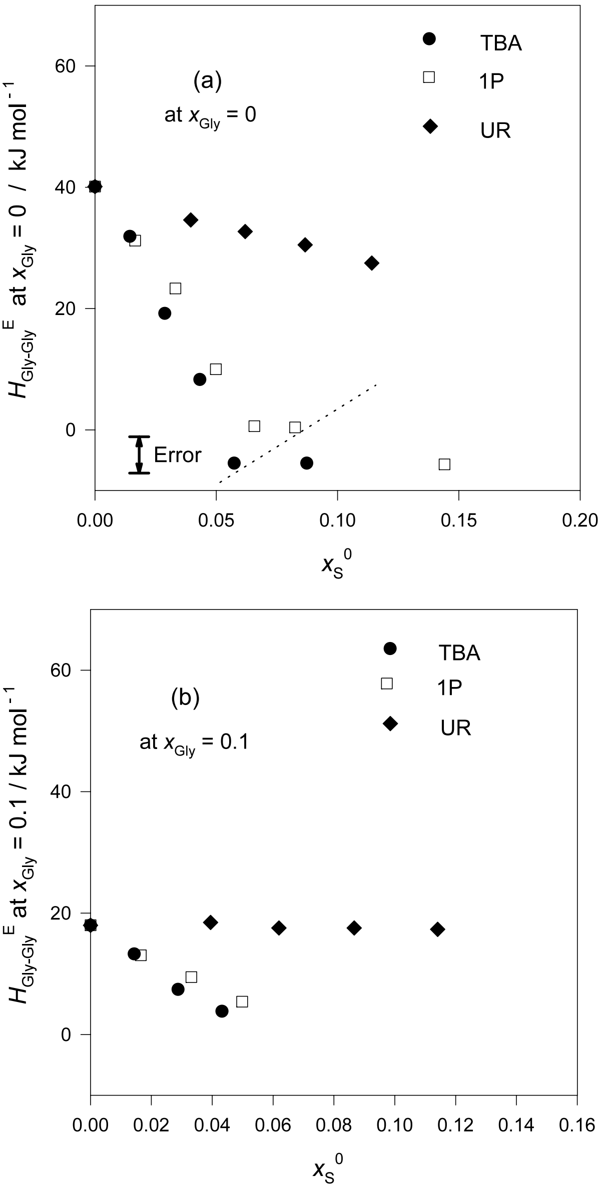


presence of Gly at $x_{\text{Gly}} = 0.1$, these effects are reduced considerably due to the presence of hydrophilic Gly.

3.2 Effects of NaF, NaCl, NaBr, NaI, and NaSCN

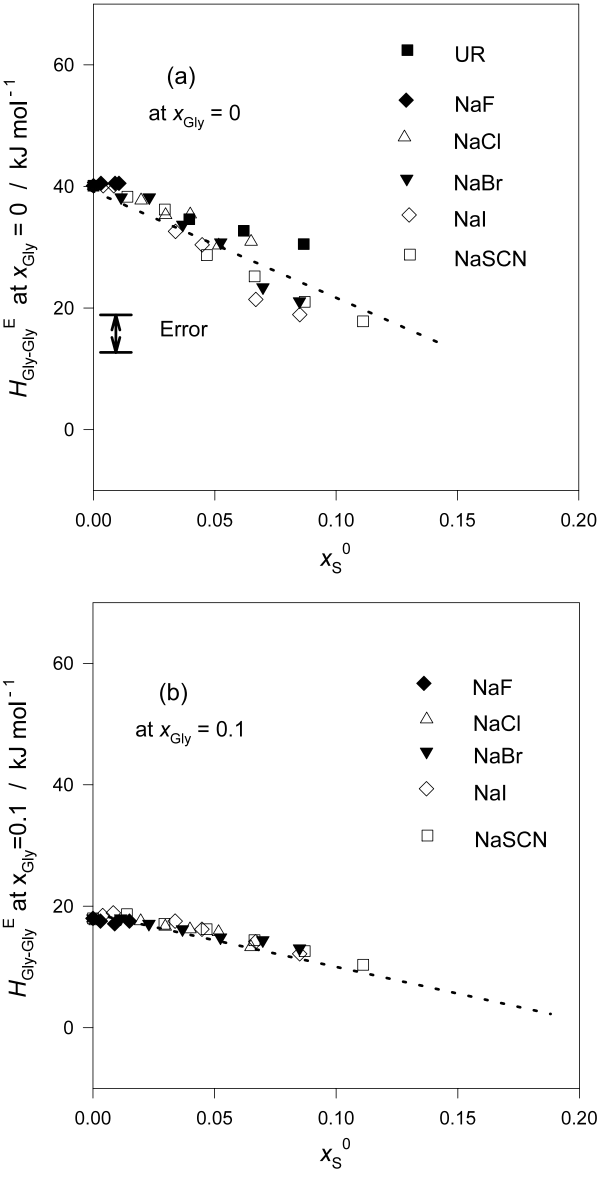
We now repeat the same procedures for Na salts of halides and SCN^- towards understanding the Hofmeister effect [23, 24]. The last ion was found to be highly hydrophilic, more so than I^-, from our previous 1P-probing work [20–22], and is ranked at a more chaotropic position than I^- in the Hofmeister series [23, 24]. Figure 6 shows the $H^{\text{E}}_{\text{Gly}}$ data. The Gly–

Fig. 5 (**a**) $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$ at $x_{\mathrm{Gly}} = 0$ for Gly–S–H_2O at 25 °C. The lower right region of the *dotted line* is outside of Mixing Scheme I for TBA and 1P. (**b**) $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$ at $x_{\mathrm{Gly}} = 0.1$ for Gly–S–H_2O at 25 °C



Gly enthalpic interaction, $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$, evaluated as above are shown in Fig. 7. Both figures are given as supplementary data. The x_{Gly}- and x^{o}_{S}-dependences of $H^{\mathrm{E}}_{\mathrm{Gly}}$ and $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$ for all salts studied are essentially similar to those for urea, Figs. 3(c), and 4(c). Figure 8 shows the x^{o}_{S}-dependences of the value of $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$ at $x_{\mathrm{Gly}} = 0$ and 0.1. Within the estimated error in $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$ shown in the figure, there is apparently no distinction among all the salts studied here. Our earlier 1P–S–H_2O studies indicated that Na^+, F^-, and Cl^- ions are hydration centers and they do not alter the bulk H_2O away from the hydration shell [12, 14, 20–22]. Furthermore, it was found that the more kosmotropic ions had higher hydration numbers [12,

Fig. 8 (**a**) $H^{E}_{Gly\text{–}Gly}$ at $x_{Gly} = 0$ for Gly–S–H_2O at 25 °C. The uncertainty is estimated as ±3 kJ·mol^{-1}. For reference the same plots for Gly–UR–H_2O are also shown. (**b**) $H^{E}_{Gly\text{–}Gly}$ at $x_{Gly} = 0.1$ for Gly–S–H_2O at 25 °C



14, 20–22], consistent with the original concept of “H_2O withdrawing power” by Hofmeister [23]. The Gly–Gly interaction in the presence of these ions occurs via bulk H_2O within Mixing Scheme I. Hence, in terms of $H^{E}_{Gly\text{–}Gly}$, the effects of these ions are small. It is expected, however, the locus of point X_{Gly} should be reduced as x_S^{o} increases, since the hydrating H_2O molecules are not available and are out of the hydrogen bond network. Unfortunately the locus of point X_{Gly} becomes less conspicuous as a test sample is added. The other ions, Br^-, I^-, and SCN^- are hydrophiles according to our earlier studies on 1P–S–H_2O, and the more hydrophilic the ion, the more chaotropic in the Hofmeister ranking [12, 14, 20–22]. As shown in Figs. 8(a) and 8(b), the effects of all the Na salts studied here seem non-existent, just as for UR shown in Figs. 5(a) and (b). Thus, two sets of different classes of ions, though the mechanism is different, do not show a clear distinction as evident in Fig. 8.

The present findings of no or little effect on $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$ for all the Na salts studied here could have an important bearing in understanding the effects of ions on biopolymers in aqueous solutions. Biopolymers are amphiphiles and have hydrophobic and hydrophilic surfaces. As pointed out above the effects of the same Na salts on the $H^{\mathrm{E}}_{\mathrm{1P-1P}}$ in the ternary 1P–S–H_2O systems were found conspicuously different between the so-called kosmotropes (F^- and Cl^-) and the chaotropes (Br^-, I^-, and SCN^-) [12, 14, 20–22]. These observations may hint that the effect of a given ion on H_2O could be insensitive to the hydrophilic part of biopolymers. The Hofmeister effect is believed to be due mainly to the distinct effect of each ion on H_2O because of its ubiquity [23, 24]. However, more recent studies tend to emphasize specific ion–protein interaction that dictates the net effect [25, 26]. Thus, the present study hints another factor to be considered as to the relative size of hydrophobic/hydrophilic surfaces of biopolymer in question towards understanding the Hofmeister series.

Supplementary Information Available

The smoothed values of the excess partial molar enthalpy of Gly, $H^{\mathrm{E}}_{\mathrm{Gly}}$, and Figs. 6 and 7, the graphs for $H^{\mathrm{E}}_{\mathrm{Gly}}$ and $H^{\mathrm{E}}_{\mathrm{Gly-Gly}}$ against x_{Gly} for Gly–S–H_2O with S = NaF, NaCl, NaBr, NaI, and NaSCN are deposited.

Acknowledgements The financial supports from the Danish Research Council and the Carlsberg Foundation are gratefully acknowledged. One of us (YK) thanks the Ministry of Education, Science, Culture and Sports, Japan, for support of the guest professorship at the Research Center for Molecular Thermodynamics, Graduate School of Science, Osaka University. During its tenure, the manuscript of this paper was first drafted.

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