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Effect of water as cosolvent in the organic phase on the partitioning of nonelectrolytes between aqueous solution and octan-1-ol[☆]

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Abstract

Enthalpies of solution at infinite dilution of propanone, tetrahydrofuran, *n*-propylamine, and tri-*n*-butylamine in water–octan-1-ol mixtures, $\Delta_{\mathrm{soln}}H^\circ$(oct–w), with water content ranging from zero to saturation have been determined. The observed trends of $\Delta_{\mathrm{soln}}H^\circ$ (oct–w) vs. the mole fraction of water are discussed and compared with the trend of the apparent molar volume of water in octan-1-ol. The connection between structural organization of water in the solvent medium and enthalpies of solution are pointed out and discussed. An attempt is also made to evaluate the observed phenomenology in terms of a preferential solvation model.

Keywords: Aqueous solutions; Calorimetry; Cosolvents; Enthalpy of solution; Nonelectrolytes; Octan-1-ol; Water–octan-1-ol mixtures

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1. Introduction

In previous papers [1,2] some thermodynamic aspects of the transfer process of simple organic solutes from infinitely dilute solution in pure octan-1-ol to infinitely dilute solution in water-saturated octan-1-ol were investigated in order to evaluate the effects of water as cosolvent in affecting the ability of octan-1-ol to extract organic

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nonelectrolytes from aqueous solutions. The results allowed us to emphasize that thermodynamic properties of solution, and hence of transfer, are strictly connected to the organization of the solvent medium. In attempting to interpret the experimental results, models in which the cosolvent water was involved in different frameworks were considered [2]. However all proposed models refer to the two opposite situations, anhydrous and fully hydrated octan-1-ol, while information about the way in which the structure of the solvent medium is modified when the water content is increased from zero to saturation is lacking. To fill this gap a solute molecule may be used as a probe of the organization of the solvent medium by considering the thermodynamic properties of solution of the solute itself in water–octanol mixtures at increasing water content. As a more general purpose this approach can furnish useful information to enable understanding of the role that water plays when it is present as cosolvent in nonpolar organic liquids and how it affects the structure and the thermodynamic stability of the solvation shell about organic solutes.

In this paper we report the results of a calorimetric determination of the enthalpies of solution at infinite dilution of a few simple organic compounds in water–octanol mixtures, $\Delta_{\mathrm{soln}}H^{\circ}$(oct–w), when the water content increases up to saturation. The picture that emerges is discussed and interpreted in terms of some simple structural models [3–7] and in terms of preferential solvation using the Kirkwood–Buff theory [8].

2. Experimental

2.1. Materials

All solutes were commercial products of the best grade available. Propan-2-one was dried over anhydrous magnesium sulfate. Tetrahydrofuran and the amines (*n*-propylamine and tri-*n*-butylamine) were refluxed over metallic sodium. All compounds were then fractionally distilled under nitrogen at atmospheric or reduced pressure. The purity of all fractions collected at constant boiling point was checked by GLC and was in all cases better than 99.8%. The collected fractions were stored before use over 4 Å molecular sieves and showed a water content $< 0.01\%$, determined by Karl Fischer titration. Octan-1-ol, a Fluka product of purissimum grade ($> 99.5\%$), was distilled under nitrogen at reduced pressure. The samples used showed a purity (GLC) better than 99.9%. Water was first deionized and then distilled from alkaline $KMnO_4$. The water octan-1-ol solvent mixtures used in the experiments were obtained by weight and for each solute at least five solvent mixtures of different water content were prepared.

2.2. Apparatus

The calorimetric measurements of heats of solution in octan-1-ol containing increasing amounts of water were performed with an isoperibol calorimeter built for this purpose and already described [2]. For each compound and for each solvent mixture at least 15 measurements were carried out in the solute concentration range 0.001–0.02 mole fraction, X_S. As for all studied solutes a linear trend of the heats of solution vs. X_S

was observed, it was always possible to linearly extrapolate in order to obtain the limiting solution enthalpies. Depending on the way the measurements are carried out, is only possible to estimate the maximum uncertainty affecting either the experimental heats of solution or the corresponding X_S values. By evaluating all the sources of error these uncertainties can be estimated as large as 0.1 kJ mol^{-1} for the values of the heat of solution and 1×10^{-5} for X_S. However the uncertainty of the limiting enthalpies of solution was usually rather lower than 0.1 kJ mol^{-1}. As an example the experimental heats of solution of tetrahydrofuran in the different water–octanol mixtures vs. X_S are reported in Fig. 1.

3. Results and discussion

The experimentally determined heats of solution at infinite dilution in water–octanol mixtures with various water contents are reported in Table 1. Plots of $\Delta_{soln}H^\circ$ (oct–w) vs. the mole fraction of water in the solvent mixture, X_w, are given in Fig. 2.

No univocal trend is observed in the explored range. Indeed, two distinct regions can roughly be distinguished. In the first (nearly up to $X_w \simeq 0.07$) a linear trend is recognized with slopes -22.9 ± 3.2, -20.05 ± 0.8, -25.59 ± 2.55, and -16.02 ± 3.35 kJ mol^{-1} for propanone, tetrahydrofuran, *n*-propylamine, and tri-*n*-butylamine, respectively. In the second region, which extends up to saturation ($X_w \simeq 0.26$ [2]), a not well defined trend is shown; however a weaker dependence of $\Delta_{soln}H^\circ$ (oct–w) values on

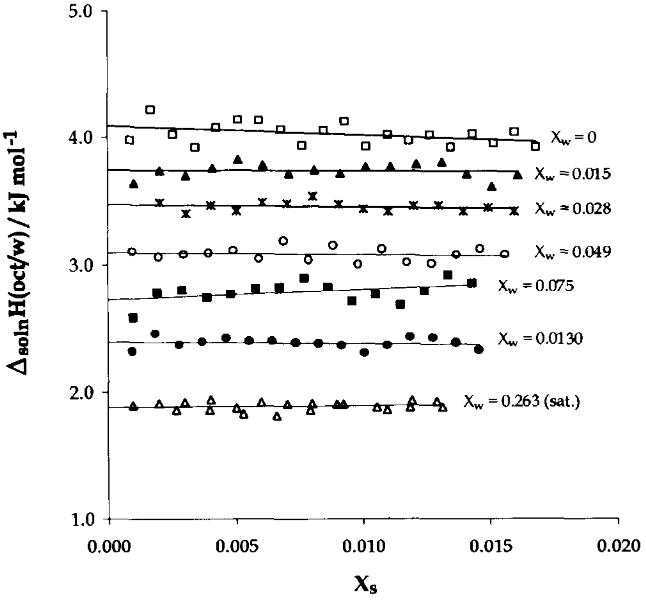

Fig. 1. Enthalpies of solution of tetrahydrofuran in water–octan-1-ol mixtures, $\Delta_{soln}H^\circ$(oct–w), vs. mole fraction of the solute, X_S.

Table 1
Limiting enthalpies of solution, $\Delta_{\mathrm{soln}}H^{\circ}$(oct–w), of some organic compounds in water–octan-1-ol mixtures at various water mole fractions, X_{w}, at 298.15 K[a]

X_{w}	$\Delta_{\mathrm{soln}}H^{\circ}$(oct–w)	b
Propanone		
0	8.91 ± 0.06[b]	-21.8 ± 5.5
0.0141	8.73 ± 0.04	-24.2 ± 3.3
0.0294	8.16 ± 0.08	-19.9 ± 7.4
0.0485	7.87 ± 0.04	-15.6 ± 3.9
0.0827	7.51 ± 0.05	-20.5 ± 4.4
0.1336	6.73 ± 0.04	-8.9 ± 4.1
0.2633	5.88 ± 0.04[b]	-8.5 ± 4.4
Tetrahydrofuran		
0	4.09 ± 0.04[b]	-7.2 ± 3.7
0.0151	3.74 ± 0.03	-0.8 ± 3.2
0.0290	3.47 ± 0.02	-2.6 ± 2.3
0.0495	3.09 ± 0.03	-1.6 ± 2.9
0.0746	2.72 ± 0.04	8.0 ± 5.0
0.1303	2.39 ± 0.02	-1.4 ± 2.5
0.2633	1.88 ± 0.02[b]	0.7 ± 2.1
n-Propylamine		
0	-8.75 ± 0.07[b]	13.5 ± 1.7
0.0142	-9.11 ± 0.16	10.9 ± 14.7
0.0283	-9.61 ± 0.11	33.1 ± 10.5
0.0485	-9.96 ± 0.04	47.7 ± 4.4
0.0750	-10.66 ± 0.06	5.0 ± 5.8
0.1286	-11.39 ± 0.08	6.4 ± 8.5
0.2633	-12.28 ± 0.08[b]	23.6 ± 10.2
Tri-n-butylamine		
0	-2.98 ± 0.03[b]	29.5 ± 1.2
0.0155	-3.52 ± 0.05	26.9 ± 13.4
0.0263	-3.81 ± 0.05	61.6 ± 13.4
0.0486	-4.07 ± 0.05	29.3 ± 16.2
0.0758	-4.27 ± 0.05	45.6 ± 16.0
0.1286	-4.60 ± 0.03	39.4 ± 9.7
0.1901	-4.64 ± 0.03	40.5 ± 9.9
0.2633	-4.64 ± 0.02[b]	7.5 ± 8.8

[a] $\Delta_{\mathrm{soln}}H^{\circ}$(oct–w) and b are the regression parameters of the relation: $\Delta_{\mathrm{soln}}H(\text{oct–w}) = \Delta_{\mathrm{soln}}H^{\circ}(\text{oct–w}) + bX_{\mathrm{S}}$, where X_{S} is the mole fraction of the solute in the solvent mixture. All data in kJ mol^{-1}. [b] Data taken from Ref. [2].

X_{w} respect to the first region is evident for all the solutes, becoming a plateau for tri-*n*-butylamine only.

An attempt to calculate the observed above mentioned slopes has been made by linearly combining the standard enthalpies of solution in water and in octan-1-ol,

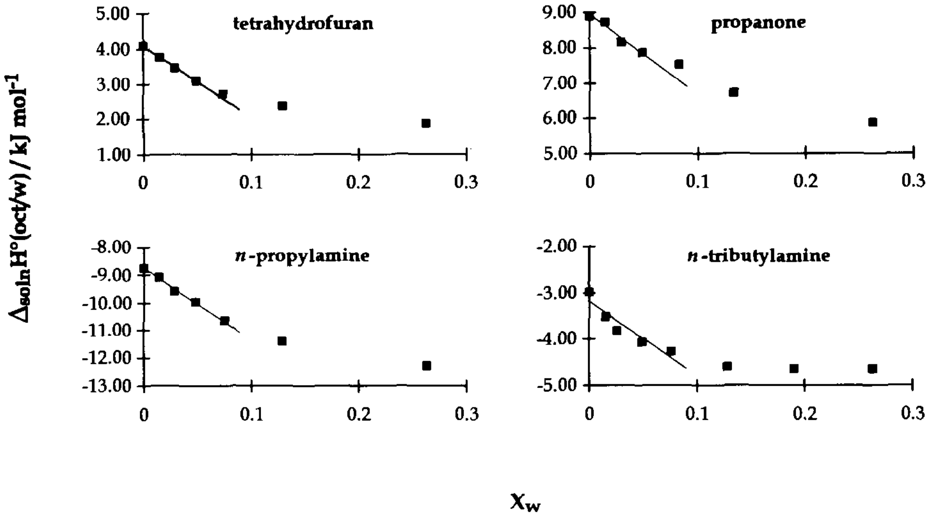

Fig. 2. Limiting enthalpies of solution in water–octan-1-ol mixtures vs. mole fraction of water, X_w.

namely:

$$\Delta_{soln}H°(\text{oct–w}) = (1 - X_w)\Delta_{soln}H°(\text{oct}) + X_w\Delta_{soln}H°(\text{w})$$
$$= \Delta_{soln}H°(\text{oct}) - \Delta_{trf}H°(\text{w} \rightarrow \text{oct})X_w \quad (1)$$

where $\Delta_{trf}H°(\text{w} \rightarrow \text{oct}) = \Delta_{soln}H°(\text{oct}) - \Delta_{soln}H°(\text{w})$. Obviously the meaning of $\Delta_{soln}H°(\text{w})$ quantity, which refers to the solution process in the water bulk, has to be clarified when employed to describe solute–water interactions in dilute solution in organic solvents. By supposing that the solution in water of an organic solute containing a hydrophilic centre occurs according to the scheme:

$$\begin{aligned} &(H_2O)_m \rightleftharpoons (H_2O)_{m-1} + H_2O && \Delta H_1 \\ &RY + H_2O \rightleftharpoons RY{\cdot}H_2O && \Delta H_2 \qquad (2) \\ &RY{\cdot}H_2O + (H_2O)_m \rightleftharpoons [RY{\cdot}H_2O]{\cdot}(H_2O)_m && \Delta H_3 \end{aligned}$$

it is reasonable to assume that $\Delta H_1 \cong -\Delta H_3$. Under this hypothesis the $\Delta_{soln}H°(\text{w})$ quantity becomes $\Delta_{soln}H°(\text{w}) \cong \Delta H_2$ and that justifies its use in Eq. (1). Therefore, according to Eq. (1), the $\Delta_{trf}H°(\text{w} \rightarrow \text{oct})$ values should correspond to the slopes of the initial range of the curves of Fig. 2.

$\Delta_{trf}H°(\text{w} \rightarrow \text{oct})$ values, calculated from $\Delta_{soln}H°(\text{oct})$ [2] and $\Delta_{soln}H°(\text{w})$ [9], are -18.53, -19.35, and -15.57 kJ mol^{-1} for propanone, tetrahydrofuran, and *n*-propylamine respectively, while no calculation is possible for tri-*n*-butylamine owing to the lack of $\Delta_{soln}H°(\text{w})$ data. This result suggests that when weakly interacting solutes (not hydrogen-bond donors) are involved, up to mole fraction of water $\simeq 0.07$ the interactions can be considered almost as a statistical average of the number of molecules of the two components surrounding the solute itself. In contrast, when a strong hydrogen-bond donor such as *n*-propylamine is considered, the observed value is 10 kJ mol^{-1} more negative than that calculated, which suggests that one of the two components of the solvent medium preferentially interacts with the solute molecule.

The linear trend is soon abandoned by all considered solutes, which agrees with the data obtained by Berti et al. in studies concerning the free energies of solvation [10] and the apparent molar volumes, Φ_V, of water in octan-1-ol [11]. In fact when these quantities are plotted vs. the mole fraction of water a trend similar to those shown in Fig. 2 is observed. As an example Fig. 3 reports the function $\Phi_V = f(X_w)$, which shows a discontinuity near $X_w \simeq 0.07$. Beyond this concentration the value of Φ_V remains constant up to saturation, indicating that water, in this concentration range, is involved every time in the same interactions framework. The "*critical*" concentration $X_w \simeq 0.07$ probably represents the value at which dramatic structural reorganization of solvent medium takes place.

It was believed for a long time that in *n*-alkanols with more than five carbon atoms the added water disrupts the framework of linear oligomers of alcohol molecules to form water-centered aggregates consisting of one water molecule and four molecules of alkanol [3–6]. This hypothesis, inferred from dielectric constant measurements and from the observation that the NMR exchange rate of hydroxylic protons with water was maximum at $X_w \simeq 0.2$, is not in agreement with recent and more conclusive observations by Francks et al. [7] based on X-ray diffraction analysis. This study has shown that pure octanol aggregates in clusters by means of polar hydroxyl groups, which can be considered to be roughly confined within spheres. When octanol becomes fully hydrated the same situation is found but the size of the clusters is increased, the added water being probably sequestred by the preexisting aggregates. The experimental data do not allow the authors to argue how many water molecules are lodged in the alcohol aggregates, but the relative large size of the polar region detected by the X-ray diffraction patterns suggests that each aggregate contains rather more than four water molecules. The hydrocarbon chains of octanol seem to be nearly fully extended and the

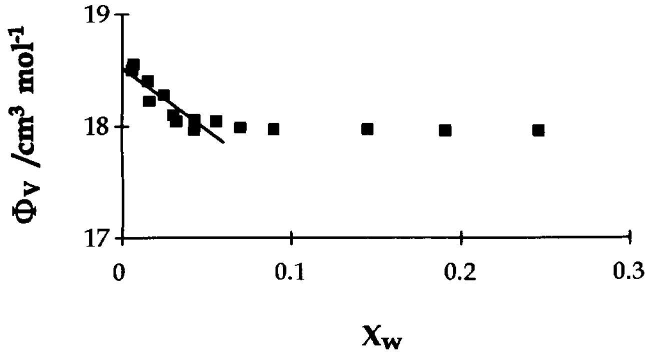

Fig. 3. Apparent molar volumes of water vs. mole fraction of water, X_w.

average distances between neighboring clusters suggest that interdigitation between chains may take place. Finally, even though there is evidence that some reorganization occurs during hydration from pure to water-saturated octan-1-ol the diffraction patterns are quite similar and hence the basic organization has to be the same.

We substantially agree with these conclusions but we want to stress that the work of Francks et al. [7] only enables the inference that no major differences are found when anhydrous and water-saturated octan-1-ol structures are compared; nothing can be inferred about the structure of the solvent medium at intermediate concentrations. Indeed data reported in the present work as well as data of Berti et al. [10, 11] seem to suggest that significant differences in the reorganization of water have to take place close to $X_w \simeq 0.07$. It could be argued that water is mainly dispersed as monomer below this concentration and only beyond this value its chemical potential is large enough to allow to water itself to force the preexisting alcohol aggregates; the value $X_w \simeq 0.07$ thus resembles a sort of critical micellar concentration.

In order to get a different point of view interpretating the observed trends we tried to deduce the local organization in water–octan-1-ol systems by applying the Kirkwood–Buff theory [8] according to the procedure of Lepori and Matteoli [12].

In a binary system information about the excess or deficiency of the two components of the mixture, say i and j, around a molecule taken as reference is included in the so-called Kirkwood–Buff integrals, G_{ij} which are integrals of the pair correlation functions. The G_{ij} functions (with i $\neq$ j) are related to the thermodynamic properties by the following relationships:

$$\begin{aligned} G_{ij} &= RT\kappa_T - \bar{V}_i \bar{V}_j / DV^* \\ G_{ii} &= G_{ij} + (\bar{V}_j/D - V^*)/x_i \\ D &= 1 + x_1 \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{T,P} \end{aligned} \tag{3}$$

where κ_T is the isothermal compressibility, $\bar{V}_i$ and $\bar{V}_j$ are the partial molar volumes of the two components, V^* is the volume per mole of mixture ($V^* = x_i \bar{V}_i + x_j \bar{V}_j$) and γ_i is the Raoult activity coefficient for component i. The $RT\kappa_T$ term can usually be neglected.

By combining free energies of solvation of water in octan-1-ol published by Berti et al. [10] and solubility data of water in octan-1-ol by Apelblat [13] and by fitting the collected data with a three-parameter Redlich–Kister equation it was possible to calculate the activity coefficient of water, γ_w, as a function of its mole fraction. Kirkwood–Buff integrals, G_{oo}, G_{ww} and G_{ow} were then calculated according to Eq. (3) by employing the partial molar volumes of Berti et al. [11] and neglecting the $RT\kappa_T$ term. From Kirkwood–Buff integrals it was also possible to calculate the δ_{ij} functions which represent the average local excess of i particles about a j particle:

$$\begin{aligned} \delta_{ii} &= x_i x_j (G_{ii} - G_{ij})/(x_i G_{ii} + x_j G_{ij} + V_{corr}) \\ \delta_{ij} &= x_i x_j (G_{ij} - G_{jj})/(x_i G_{ij} + x_j G_{jj} + V_{corr}) \end{aligned} \tag{4}$$

where x_i and x_j are the bulk mole fractions and V_{corr} is the correlation volume (i.e. the volume in which correlation effects are recognizable) estimated to be as large as 5000 cm^3.

In Fig. 4a are plotted the Kirkwood–Buff integrals, G_{ij}, for the water–octanol system and in Fig. 4b are plotted the corresponding δ_{ij} functions. It can be observed that the G_{ww} function increases in the whole range and its derivative is larger when saturation is approached. Correspondingly the δ_{ww} function increases to 0.13 at saturation. This value is quite high thus showing a strong tendency of water molecules to homocoordinate. In contrast the δ_{ow} function decreases with water concentration and again this opposes the hypothesis of stable well-defined water(octanol)$_4$ aggregates. Finally, the δ_{wo} function increases only slightly with water concentration. Again this behavior would strengthen the hypothesis of preexisting aggregates created by the polar hydroxylic group of octanol into which water molecules can be lodged as well as happens in inverse micellar systems.

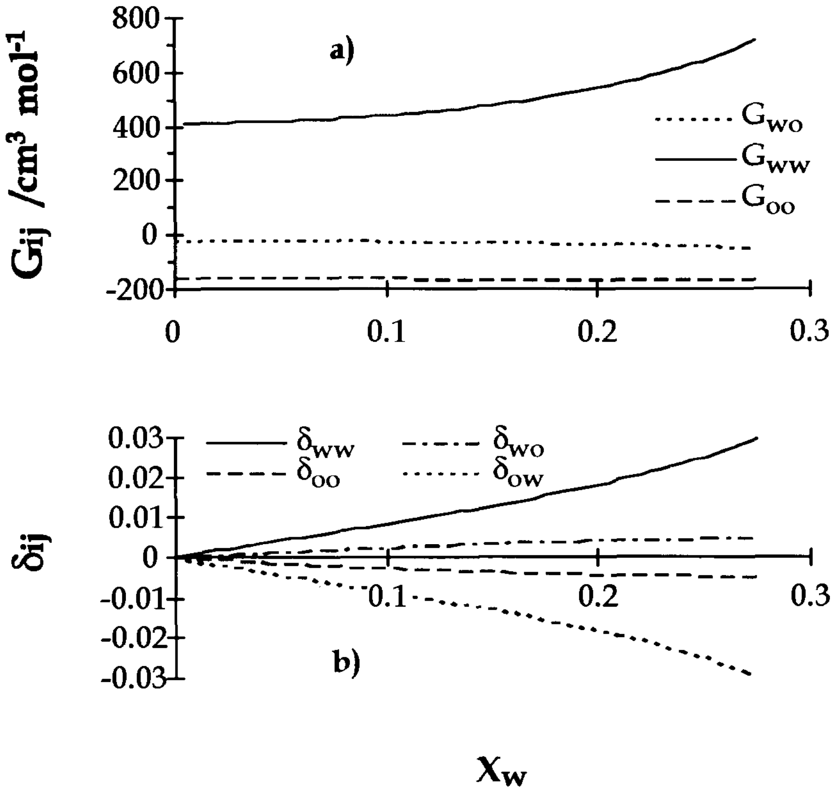

Fig. 4. Binary water–octan-1-ol system: a) Kirkwood–Buff integrals, G_{ij}, b) mean local excess, δ_{ij}.

4. Conclusion

From analysis of the trend of the limiting enthalpies of solution of simple monofunctional organic solutes in binary water–octanol mixtures vs. X_w, it was possible to recognize two different arrangements of water in the solvent medium which reflect on the solute–solvent interactions. The first situation, operative in the X_w range up to $\simeq 0.07$, produces a linear decrease of the $\Delta_{soln}H^\circ$(oct–w) values, when X_w increases. Such a decrease is more pronounced than that evaluable by assuming additive character for the solute–octan-1-ol and solute–water interactions. The second situation, operative for X_w ranging from 0.07 to the saturation value of 0.26, produces only a feeble decrease of $\Delta_{soln}H^\circ$(oct–w) with the X_w increase. This result indicates that a very different state of water is realized in octanol at higher water content compared with that at lower water concentrations. This second state is cooperatively achieved when the concentration of water is larger than the "*critical*" value of $X_w \simeq 0.07$ and is maintained up to phase demixing. Comparison of the quoted trends of $\Delta_{soln}H^\circ$(oct–w) vs. X_w with the corresponding trends of free energies and apparent molar volumes of water in octanol shows that at infinite dilution the monofunctional organic solutes are effective probes of the state of water in water–octanol mixtures. X-ray diffraction analysis of these mixtures as well as the application of the Kirkwood–Buff theory suggest that for X_w ranging from zero to 0.07 water is probably present in a monomeric form. When X_w increases up to 0.26 water clusters are formed and included in largely pre-existing clusters of octanol molecules.

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