Enthalpies of solution of methoxy and ethoxy end group oligomers of poly(ethylene glycol) in binary solvent water—dimethylformamide
Study of hydrophobic hydration

P. CIFRA and A. ROMANOV

Polymer Institute, Centre for Chemical Research, Slovak Academy of Sciences, CS-842 36 Bratislava

Deviations from ideality in solution enthalpies of solutes are explained by hydrophobic hydration. The extent of this type of hydration is expressed by means of two methods. Experimental results obey previously proposed group contribution concept for evaluation of enthalpic effect of hydrophobic hydration and the obtained methylene group contribution is in good agreement with that obtained previously from the data on other hydrophobic homologous series.

Наблюданные отклонения от идеальности в энтальпиях растворения растворяемых соединений объясняются гидрофобной гидратацией. Мера этого типа гидратации выражается при помощи двух методов. Экспериментальные результаты соответствуют предложенной раннее аддитивной концепции групповых вкладов в гидрофобную гидратацию. Наблюданный вклад метиленовой группы в согласии с величиной полученной из данных касающихся других гидрофобных гомологических рядов.

The hydrophobic effect is recently often studied phenomenon in connection with its presence and decisive role in micellar solutions, liquid chromatography with reversed phase, oil recovery processes by means of surfactants and polymers, biological systems *etc.* and also from the theoretical point of view [1, 2]. Hydrophobic effect (*i.e.* hydrophobic hydration and hydrophobic interaction) as known has its origin in stronger hydrogen bonding between water molecules in vicinity of apolar groups of solute molecule in water in comparison with water molecules in bulk water far from solute.

This is a contribution to quantitative evaluation of hydrophobic hydration (further HH) since the extent of HH of solute is a necessary condition to form hydrophobic association. As hydrophobic solutes we have chosen alkyl end group oligomers of poly(ethylene glycol) which are suitable for evaluation of methylene group contribution to HH. HH effect is here studied by means of measuring solution enthalpies of hydrophobic solutes in mixture of water and an aprotic cosolvent. In this mixed solvent the HH effect can be separated from

the overall effect present in dissolution process. The extent of HH effect is estimated according to the method of *Somsen* [3, 4] and method proposed in our previous publication on this subject [5].

Experimental

Diethylene glycol diethyl ether ((EG)$_2$—DEE), diethylene glycol dimethyl ether ((EG)$_2$—DME), tetraethylene glycol dimethyl ether ((EG)$_4$—DME) (Fluka A.G., Switzerland), triethylene glycol dimethyl ether ((EG)$_3$—DME) (Merck-Schuchardt, GFR), all of reagent grade purity were kindly supplied by producers and were used without further purification. *N*,*N*-Dimethylformamide (DMF) (Lachema, Brno) was dried over P$_2$O$_5$ and distilled under reduced pressure. Redistilled water was used and solutions were prepared by mass.

Enthalpies of solution to infinite dilution of solutes were measured on Calvet-type isothermal twin calorimeter [6]. The calorimeter was calibrated by Joule effect. The solute ($\approx$ 5 mg) was spread as a film on horizontal disc and placed in the container on the bottom of the calorimetric cell (12 cm in height, 1 cm on diameter, solvent volume 6 cm^3) sealed by Teflon-stopper. After the thermal equilibration the disc was placed at the top of cell. The location of the film in the cell ensures that the solution undergoes self-dilution, and makes agitation unnecessary. Response time of the calorimeter for film dissolution was comparable with the response time for mixing two liquids. After the response had disappeared we performed a control mixing to check the solution homogeneity.

Correction to vaporization enthalpies was not necessary. Calorimetric peaks were integrated by integrator (Research Institute for Macromolecular Chemistry, Brno). Enthalpies of solution were measured with standard deviation $\pm$ 0.4 kJ mol^{-1} and all heat effects were obtained at (298.1 $\pm$ 0.1) K.

Results and discussion

In enthalpies of solution a pronounced endothermal shift was observed as soon as a small amount of aprotic cosolvent was added to water, which is a characteristic feature of HH. All data on solution enthalpies of solutes are collected in Table 1.

A. The enthalpic effects of HH were obtained by the method of *Somsen* [3]. According to his statistical model the deviation of enthalpy of solution from ideal linear dependence on solvent composition of binary solvent consisting of water and aprotic cosolvent can be described by

$$\Delta(\Delta_{\text{sol}} H^\circ) = \Delta H^\circ_{\text{HH}}(x^N - x) \tag{1}$$

where $\Delta H^\circ_{\text{HH}}$, N are the enthalpic parameter of HH and the number of water molecules in the hydration cage; x is the mole fraction of water in the binary

Table 1

Solution enthalpies, $\Delta_{sol}H°$, of oligoethylene glycols as functions of composition of binary solvent H_2O—DMF at (298.1 ± 0.1) K

(EG)$_2$—DME		(EG)$_2$—DEE		(EG)$_3$—DME		(EG)$_4$—DME	
x	$\dfrac{\Delta_{sol}H°}{\text{kJ mol}^{-1}}$	x	$\dfrac{\Delta_{sol}H°}{\text{kJ mol}^{-1}}$	x	$\dfrac{\Delta_{sol}H°}{\text{kJ mol}^{-1}}$	x	$\dfrac{\Delta_{sol}H°}{\text{kJ mol}^{-1}}$
1.000	−26.31	1.000	−34.26	1.000	−38.82	1.000	−42.60
0.895	−13.85	0.900	−17.45	0.900	−19.87	0.900	−22.52
0.792	−5.76	0.786	−4.40	0.786	−9.05	0.786	−8.80
0.683	−0.55	0.692	+1.52	0.692	−2.58	0.692	−1.82
0.588	+1.30	0.495	+2.95	0.592	+0.55	0.592	+1.31
0.486	+2.13	0.295	+1.64	0.492	+0.80	0.492	+2.53
0.280	+0.83	0.000	0.05	0.295	−1.00	0.295	+1.22
0.000	−1.13			0.000	−3.35	0.000	−1.20

x — mole fraction of H_2O in the binary solvent.

Table 2

Parameters of hydrophobic hydration of solutes according to individual methods

Solute	A(1)		A(2)		B
	$\dfrac{-\Delta H°_{HH}}{\text{kJ mol}^{-1}}$	N	$\dfrac{-\Delta H°_{HH}}{\text{kJ mol}^{-1}}$	N	$\dfrac{-h_{HH}}{\text{kJ mol}^{-1}}$
(EG)$_2$—DME	34.2	4.6	35.4	9.1	148.5
(EG)$_2$—DEE	42.7	5.5	43.6	11.1	226.9
(EG)$_3$—DME	46.0	5.2	47.1	10.4	229.9
(EG)$_4$—DME	51.6	5.0	53.1	10.0	249.5

solvent. Parameters $\Delta H°_{HH}$, N were evaluated also by the modified method [4] where nonrandomness during the hydration cage formation is taken into account. Factor x^N in the previous relation is then replaced by

$$P(N) = \prod_{i=1}^{N} [x(N-1) + i - 1]/(i-1) \tag{2}$$

Resulting parameters of HH according to the original and modified method are shown in Table 2.

B. Besides the mentioned Somsen's method there are evidently also other theoretical approaches yielding the enthalpy of solution of the solute in binary solvent. *Bertrand et al.* [7, 8] relates the enthalpy of solution in binary solvent consisting of two nearly ideal solvents to excess enthalpy of solvent pair. For

larger solute molecules we can apply methods based on Flory—Huggins theory or on Prigogine—Flory—Patterson equation of state theory for expressing the solution enthalpy in binary solvent [9, 10]. However, all these relations may fail or can be completely overshadowed by specific solvation or structuralization of solvent. This is also the case of hydrophobic effect and so we use here rather the simple Somsen's method or another related method based on h_{HH} parameter (see further on).

All solution enthalpies in this paper are treated as enthalpies of solvation for the following reason. Actually the total enthalpy of dissolution of the solute into the solvent can be separated into separation contribution (enthalpy of vaporization or lattice enthalpy) and a proper interaction with solvent

$$\Delta_{sol} H^{\circ} = \Delta_{sep} H^{\circ} + \Delta_{int} H^{\circ}$$

Effect of hydrophobic hydration is, however, expressed from deviation from ideality in dependence of $\Delta_{sol} H^{\circ}$ on the composition of binary solvent and so $\Delta_{sep} H^{\circ}$ is already separated out in the case of obtaining parameter ΔH°_{HH} (or parameter h_{HH}, as shown further). The value of $\Delta_{int} H^{\circ}$ can be also further separated into an enthalpy of cavity formation and the solvation enthalpy. The enthalpy of cavity formation in water is however almost zero [11] and so in the case of using h_{HH} parameter which is obtained in the limit of composition of solvent to pure water we actually obtain only the effect of solvation.

Previously we proposed [5] another parameter to represent the extent of HH and gave several theoretical and practical arguments for this proposal. New parameter h_{HH} is defined as the limiting slope to $\Delta_{sol} H^{\circ}$ for solvent composition approaching zero cosolvent mole fraction

$$h_{HH} = -\frac{\partial \Delta_{sol} H^{\circ}}{\partial x_Y} (x_Y \to 0) \tag{3}$$

where x_Y is the mole fraction of the cosolvent in binary solvent. Parameter h_{HH} is closely related to enthalpic pairwise interaction coefficient from *McMillan —Mayer*'s theory [12]. According to this theory the change of enthalpy for dissolution of one mole of X in aqueous solution of Y is given by

$$\Delta_{sol} H^{\circ}(X \text{ in } Y + W) = \Delta_{sol} H^{\circ}(X \text{ in } W) + 2h_{XY} m_Y + 3h_{XYY} m_Y^2 + \tag{4}$$

where m_Y is the molality of Y and h_{XY} is the pairwise interaction coefficient followed by higher-order coefficients.

Parameter h_{XY} is related to our parameter h_{HH} by simple relation

$$h_{XY} = -(1/2) h_{HH} M \tag{5}$$

where M is molar mass of water. Parameter h_{XY} can be composed of group contributions of interacting molecules according to the *Wood—Savage* [13] principle

$$h_{XY} = \sum_{i,j} N_i(X) \, N_j(Y) \, H_{ij} \qquad (6)$$

where i, j are groups on interacting molecules X, Y. Owing to the validity of eqn (5) we can compose also parameter h_{HH} of group contributions by modification of relation (6)

$$h_{HH} = u + N(CH_2) \, h(CH_2) + N(CH_3) \, h(CH_3) + \qquad (7)$$

Here we do not divide Y into groups since the choice of Y is not important in this quantification of HH. The role of cosolvent Y is limited only to diluting of water. The only limitation put on the choice of Y is not to have characteristic features of water, *i.e.* not to be hydrogen-bonded solvent.

Parameter h_{HH} gives better representation of HH than is that by means of previous two parameters $\Delta H°_{HH}$, N since it is more sensitive, it can be composed of group contributions according to the McMillan—Mayer theory and Wood —Savage group contributions concept, and describes the HH of the whole molecule instead of $\Delta H°_{HH}$ which measures the HH mainly on α-C atom attached to polar group as was shown [5] by correlating of both parameters with the total molecular surface areas of hydrophobic solutes. Obtained h_{HH} parameters are shown in Table 2.

We applied the group contributions concept to the obtained individual group contributions from experimental h_{HH} parameters. Since distinguishing between methyl end group and methylene groups did not improve the correlation we considered only the number of single-type saturated carbon atom groups $N(CH_2)$ and the number of etheric groups $N(O)$. Corresponding group contributions are $h(CH_2)$ and $h(O)$, respectively. Applying multiple linear regression analysis we obtained the following group contributions: $h(CH_2) = -(34.9 \pm 9.9)$ kJ mol^{-1}, $h(O) = (17.9 \pm 20.6)$ kJ mol^{-1}. These group contributions represent experimental h_{HH} value with correlation coefficient $r = 0.992$.

The methylene group contribution to HH is in agreement with the previously obtained [5] $h(CH_2) = -(35.0 \pm 2.0)$ kJ mol^{-1} from the data on tetraalkylammonium bromides, alcohols, alkyl- and dialkylamines as hydrophobic solutes. Obtained value of $h(CH_2)$ also supports evaluated [5] fraction of hydration spheres which are affected when hydrophobic association between two methylene groups is formed.

It must be also mentioned that in previous studies on hydrophobic hydration were predominantly studied molecules with one polar group. Here we present

results on HH of molecules with several polar groups per molecule separated by ethylene groups. From the above-presented results it is clear that polar etheric groups are not influenced by each other within the molecule. It was not necessary to account for this interaction of polar groups in group contribution scheme by adding correction term as it is necessary elsewhere [14]. Thus we can conclude that the presence of more than one polar group per molecule does not affect observable HH properties of methylene groups.

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