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Enthalpies of dilution of formamide in aqueous alcohol solutions at 298.15 K

Rui Zhang, Xu Wang, Weidong Yan [*]

Department of Chemistry, Zhejiang University, Hangzhou 310027, China

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Abstract

Enthalpies of dilution of formamide in aqueous *n*-propanol, 1,2-propanediol and glycerol solutions have been determined by isothermal calorimetry at 298.15 K. The values of dilution enthalpy were used to determine homogeneous enthalpic interaction coefficients which characterize the interactions of formamide in alcohol solutions. The variations of the enthalpic pairwise interaction coefficients with the mass fraction of alcohol in mixtures are interpreted in terms of solute–solute and solute–solvent interactions.

Keywords: Enthalpies of dilution; Formamide; Aqueous alcohol solutions; Calorimeter

1. Introduction

Protein hydration is responsible for stabilizing the native structure of globular proteins in aqueous solutions [1,2]. One useful approach that assists in our understanding of these interactions is to study small molecule-water interactions [3]. Amide solutions in water and in mixed solvents are useful for modeling the fragments of biological molecules [4,5]. Alcohol water mixtures as solvents are important because of their mixed hydrophobic–hydrophilic character.

The enthalpic interaction coefficients, derived from the virial expansion of an excess thermodynamic property [6], are measures of intermolecular interactions in solution and depend significantly on variation in solvent. As a continuation of our work [7,8], the present study examines the homogenous enthalpic interaction coefficients of formamide in aqueous *n*-propanol, 1,2-propanediol and glycerol solutions.

2. Experimental

2.1. Materials and sample preparation

Formamide (AR) was kept over $CaCO_3$ overnight and then distilled twice at reduced pressure. *n*-Propanol (AR), 1,2-propanediol (AR) and glycerol (AR) were distilled, respectively, under atmospheric pressure with middle fraction collected. All of the purified products were stored over P_2O_5 in a desiccator before use. The water used for the preparation of solutions was deionized and distilled using a quartz sub-boiling purifier.

Both the aqueous solutions, which were used as mixed solvents (water + alcohol), and the formamide solutions (formamide + alcohol + water) were prepared by mass with a Mettler AE 200 balance. All the solutions were degassed and used within 12 h after preparation.

2.2. Calorimetric procedure

The enthalpies of dilution were measured with an isothermal calorimeter (model 4400 IMC, Calorimeter Science Corporation, USA) at 298.15 K. The flow-mixing system is comprised of two CSC 4442 flow-mixing cells [9,10] and two syringe pumps (model: 260D, ISCO Inc., USA). The IMC data acquisition software was provided by Calorimetry Sciences Corporation. The scheduler/monitor program of pumps was developed by our group. The variation in flow rates of the syringe pumps is less than 0.2%. The flow rates were determined by weighing the masses of liquids through the pump with 5 min. The relative mean deviation of thermal powers determined was 0.3%. Details of testing of the calorimeter were reported elsewhere [11].

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[*] Corresponding author. Tel.: +86 571 87951430; fax: +86 571 87951895.
E-mail address: yanweidong@zju.edu.cn (W.D. Yan).

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The enthalpies of dilution $\Delta_{\text{dil}}H_{\text{m}}$ can be obtained by the following equation [12]

$$\Delta_{\text{dil}}H_{\text{m}} = \frac{P(1+m_{\text{i}}M_2)}{m_{\text{i}}f_2} \tag{1}$$

where P is the dilution thermal power in watts, m_{i} is the concentration of the initial solution (mol kg^{-1}), M_2 is the molar mass of formamide (kg mol^{-1}), f_2 is the flow rate of formamide solution (kg s^{-1}). The uncertainties of all $\Delta_{\text{dil}}H_{\text{m}}$ values owing to duplicate runs at each initial molality and the slight variations of flow rates are within 1%. The concentration of the final solution, m_{f} was calculated from the equation

$$m_{\text{f}} = \frac{m_{\text{i}}f_2}{f_1(m_{\text{i}}M_1+1)+f_2} \tag{2}$$

where f_1 is the flow rate of diluent (aqueous alcohol solution), M_1 is the molar mass of diluent (kg mol^{-1}).

3. Results and discussion

The thermodynamic formalism for the treatment of the enthalpies of dilution is based on the excess enthalpy concept [13,14]. If aqueous alcohol solution is regarded as solvent, the excess enthalpy per kg of solvent (H^{E}) of a solution containing formamide at molality m is given by

$$H^{\text{E}} = h_2m^2 + h_3m^3 + h_4m^4 + \cdots \tag{3}$$

where h_2, h_3, h_4, etc. are enthalpic pairwise, triplet and quadruplet interaction coefficients, respectively. The molar enthalpy of dilution ($\Delta_{\text{dil}}H_{\text{m}}$) of the solution from an initial molality (m_{i}) to a final molality (m_{f}), is therefore given by

$$\begin{aligned}\Delta_{\text{dil}}H_{\text{m}} &= H_{\text{m}}^{\text{E}}(m_{\text{f}}) - H_{\text{m}}^{\text{E}}(m_{\text{i}})\\ &= h_2(m_{\text{f}}-m_{\text{i}})+h_3(m_{\text{f}}^2-m_{\text{i}}^2)+h_4(m_{\text{f}}^3-m_{\text{i}}^3)+\cdots\end{aligned} \tag{4}$$

The experimental values of $\Delta_{\text{dil}}H_{\text{m}}$ of formamide in aqueous n-propanol, 1,2-propanediol and glycerol solutions together with the initial and final molalities are listed in Tables 1–3 in supplementary data. This data were fitted to Eq. (4) by a least-squares procedure to obtain the h coefficients (Tables 1–3). As there are some difficulties in the interpretation of higher coefficients [15], only the pairwise coefficient h_2 is considered. The h_2 values of formamide in pure water is −104.68 J kg mol^{-2}, which is in good agreement with the literature value [16]. The difference from the literature [17] results from a different experimental approach and concentration range.

Table 1
Enthalpic interaction coefficients of formamide in aqueous n-propanol solutions at 298.15 k

w (n-propanol)	h_2[a] (J kg mol^{-2})	m_{i} (mol kg^{-1})	r
0.0000	−104.68 (9.88)	2.9581	0.9998
0.0500	−158.75 (16.60)	3.0118	0.9999
0.1000	−297.48 (18.95)	3.0037	0.9999
0.1500	−396.30 (45.18)	2.9948	0.9998
0.2000	−471.06 (39.76)	3.0010	0.9998
0.2500	−408.97 (44.72)	3.0044	0.9997
0.3000	−303.04 (10.88)	2.9893	0.9999

[a] The values in parentheses are the uncertainties of h_2.

Table 2
Enthalpic interaction coefficients of formamide in aqueous 1,2-propanediol solutions at 298.15 k

w (1,2-propanediol)	h_2[a] (J kg mol^{-2})	m_{i} (mol kg^{-1})	r
0.0000	−104.68 (9.88)	2.9581	0.9998
0.0500	−129.10 (21.30)	3.0016	0.9997
0.1000	−253.37 (13.15)	2.9986	0.9999
0.1500	−283.71 (27.53)	2.9921	0.9997
0.2000	−351.24 (26.02)	2.9940	0.9998
0.2500	−272.41 (26.02)	3.0006	0.9998
0.3000	−237.85 (22.93)	2.9913	0.9999

[a] The values in parentheses are the uncertainties of h_2.

Table 3
Enthalpic interaction coefficients of formamide in aqueous glycerol solutions at 298.15 K

w (glycerol)	h_2[a] (J kg mol^{-2})	m_{i} (mol kg^{-1})	r
0.0000	−104.68 (9.88)	2.9581	0.9998
0.0500	−121.02 (16.58)	2.9567	0.9997
0.1000	−193.11 (13.44)	2.9829	0.9998
0.1500	−154.03 (19.82)	2.9946	0.9997
0.2000	−149.55 (21.28)	2.9705	0.9997
0.2500	−133.58 (20.50)	2.9891	0.9997
0.3000	−144.46 (24.17)	3.0038	0.9997

[a] The values in parentheses are the uncertainties of h_2.

From Fig. 1, the enthalpic pairwise interaction coefficients of formamide are all negative in aqueous alcohol solutions and pass through a minimum at different concentrations. The h_2 coefficients of formamide increase in the sequence: n-propanol < 1,2-propanediol < glycerol. With the increase in hydroxyl groups, the minimum shifts to lower concentrations.

For formamide, which has no alkyl groups, dipole-dipole interactions dominate the pair-wise interaction of formamide in pure water and these interactions are expected to result in a negative contribution to h_2 [17,18].

Since the h_2 coefficient relates closely to the solvent-mediated interactions between two solvated molecules [19], the

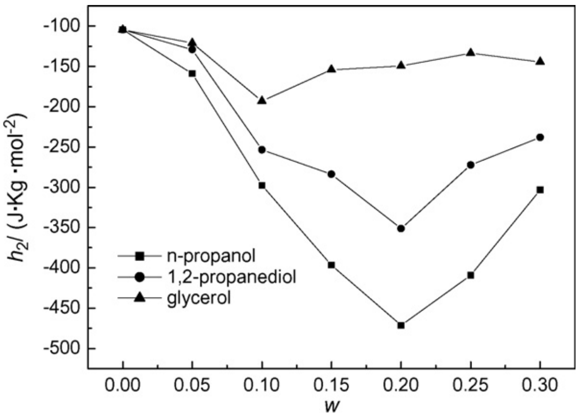

Fig. 1. The variations in h_2 of formamide with the mass fractions of alcohol in mixed solvents at 298.15 K.

energetic effect arising from changes in the solvent structure in the vicinity of the dissolved particles leads to the variations in h_2 coefficients in the mixed solvents. In the ternary solutions under investigation (formamide + alcohol + water), the overall effect on h_2 reflects the equilibrium among the following superimposed processes: The dipole–dipole interaction between two formamides is exothermic effect, which leads to a negative contribution to h_2. Interaction between formamide and the alcohol is exothermic effect, which lead to a negative contribution to h_2. An endothermic process between formamide and the alky groups of alcohol is counteracted by an exothermic process between formamide and the hydroxyl groups of alcohol. A partial dehydration of the hydration shell of formamide and alcohol molecule is an endothermic process, which lead to a positive contribution to h_2. The positive values of the h_2 coefficients were interpreted as due to the prevailing release of structured water from the hydration cospheres to the bulk.

In alcohol solutions, the exothermic process predominates over endothermic processes, resulting in negative values of h_2 for formamide. The predominance increases gradually with the increasing concentration of alcohol in the mixtures. The effect is the most prevailing at different concentrations of the cosolutes, leading to a minimum of h_2 coefficients. With introduction of second or third hydroxyl group on the monohydric alcohol, their interactions with formamide increase, giving a more negative contribution to h_2. The influence of alcohols on water depends mainly on number of hydroxyl group in an alcohol molecule [20]. The polyhydric alcohol-water interactions are stronger than the monohydric alcohol-water interactions. This causes an increase in the endothermic effect of the partial dehydration of alcohol, which give a more positive contribution to h_2 in polyhydric alcohol solutions than in *n*-propanol solutions. Desonyers and co-workers [21] gave a general discussion for structural interactions, and thought that structural interactions make quite a large contribution to the enthalpic function, and sometimes surpass the effect of other interactions [22,23].

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.10.006.

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