Enthalpic and volumetric studies of the interactions of butanamide in aqueous alkan-1-ol solutions at 298.15 K

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Abstract

Enthalpies of solution and apparent molar volumes have been investigated for butanamide in aqueous methanol, ethanol and propanol solutions. Enthalpic and volumetric interaction coefficients have been calculated by a least-squares method. Pair interaction coefficients are discussed from the perspective of dipole–dipole and structural interactions. Triplet interaction coefficients are interpreted by the solvent separated association pattern.
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1. Introduction

As model compounds of polypeptides [1,2], amides play an important role in understanding the conformational stability of proteins and providing insights into physiochemical phenomena [3,4]. Amide + alkan-1-ol mixtures could give much information about solute–solute and long-range intramolecular interactions. The authors have reported the enthalpic and volumetric interactions of formamide with alcohol in water at 298.15 K [5]. The present paper further presents the enthalpic and volumetric interactions of butanamide in aqueous alkan-1-ol solutions at 298.15 K.

2. Experiment

Methanol (A.R.), ethanol (A.R.) and propanol (A.R.) were distilled under atmospheric pressure with middle fraction collected. Butanamide (A.R.) was recrystallized from acetone + water mixtures and dried under vacuum for 24 h. All of the purified products were stored over P_2O_5 in a desiccator before use. The water used in this experiment was deionized and redistilled.

Enthalpies of solution were measured at 298.15 K in a C-80 calorimeter (Setaram) using reversed-mixing vessel, which has two chambers separated by a tilting lid. In order to obtain a complete separation of the chambers, 0.5 g mercury was put into the vessel to seal the gap between the vessel and the lid. Butanamide was weighed on a single-pan balance (Mettler) to $\pm 10\,\mu g$. About 0.05–0.3 g butanamide was introduced into the vessel and the lid was put in place. About 5 ml solvent was weighed to ± 0.1 mg. The calibration of the calorimeter was performed with an EJ2 Joule-effect device (Setaram). The total uncertainty in the measurement was about $\pm 0.5\%$.

Densities of solution were measured at 298.15 K with a vibrating-tube digital density meter (Model 60/602, Anton Paar). The temperature around the density meter cell was controlled by circulating water from a constant-temperature bath (Schott, Germany). A CT14500 temperature controller and a CK-100 ultracryostat were employed to maintain the bath temperature at 298.15 ± 0.005 K. The density meter was calibrated daily with dry air and deionized water. The density of pure water at 298.15 K was taken as $0.99705\,\mathrm{g\,cm^{-3}}$ [6]. Reproducibility of the density measurements was better than $\pm 3 \times 10^{-6}\,\mathrm{g\,cm^{-3}}$.

3. Theoretical relations

According to McMillan and Mayer approach [7], all the thermodynamic properties of multi-component solutions can be

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expressed by using an expansion in m (where m is the molalities defined per kilogram of pure water), which relates to the non-ideal contributions of any total thermodynamic function to a series of pair, triplet and higher-order interaction coefficients. The enthalpies of transfer of butanamide (b) from pure water (w) to alkan-1-ol solutions (a) can be expressed as [8,9]. For the system studied here, the truncated form of the equation as [9] is used:

$$\frac{\Delta_{tr}H_b(w \rightarrow w+a)}{m_a} = 2h_{ab} + 3h_{abb}m_b + 3h_{aab}m_a \quad (1)$$

where h_{ab} is the heteroactic enthalpic pair interaction coefficients, and h_{abb}, h_{aab} are the enthalpic triplet interaction coefficients.

Apparent molar volumes of butanamide in pure water were calculated by using following equation:

$$\Phi_{Vb} = \frac{M_b}{\rho} - \frac{\rho - \rho_0}{m_b\rho\rho_0} \quad (2)$$

Where M_b and m_b are, respectively, the molar mass and the molality of butanamide and ρ, ρ_0 are, respectively, the densities of solution and water. In ternary systems butanamide + alkan-1-ol + water, the apparent molar volumes of butanamide Φ_{Vb} can be calculated as

$$\Phi_{Vb} = \frac{1 + m_aM_a + m_bM_b}{m_b\rho} - \frac{1 + m_aM_a}{m_b\rho_0} \quad (3)$$

where m_a and m_b are the molalities defined per kilogram of pure water, ρ the densities of the ternary aqueous solution and ρ_0 is the density of alkan-1-ol + water binary solution. Just as the transfer enthalpy in Eq. (1), the standard transfer volumes of butanamide from pure water to aqueous alkan-1-ol solutions can be expressed as follows:

$$\Delta_{tr}\Phi_{Vb}\frac{w \rightarrow w+a}{m_a} = 2V_{ab} + 3V_{abb}m_b + 3V_{aab}m_a \quad (4)$$

where V_{ab} is the volumetric pair interaction coefficients and V_{abb}, V_{aab} are the volumetric triplet interaction coefficients.

4. Results and discussions

The measured enthalpies of solution of butanamide in water and in aqueous methanol, ethanol, propanol solutions are given, respectively, in supplementary Tables 1–4. And the densities of solution of butanamide in pure water and in aqueous alkan-1-ol solutions at 298.15 K are given, respectively, in supplementary Tables 5–8. The apparent molar volumes of butanamide in pure water are found to be a linear function of the amide molality over the molality range studied. The molar enthalpies of solution and

Table 1
The enthalpic interaction coefficients of butanamide with methanol, ethanol and propanol in aqueous solutions at 298.15 K

Alkan-1-ol	h_{ab} (J kg mol^{-2})	h_{abb} (J kg^2 mol^{-3})	h_{aab} (J kg^2 mol^{-3})
Methanol	425 ± 3	18 ± 3	5 ± 1
Ethanol	649 ± 6	21 ± 7	29 ± 1
Propanol	894 ± 8	27 ± 11	88 ± 3

±n is the S.E.

the apparent molar volumes of butanamide in pure water can be expressed by the following equations:

$$\Delta H_m \text{ (J mol}^{-1}) = 9083 + 609m_b \quad (\text{S.D.} = 6) \quad (5)$$

$$\Phi_{Vb} \text{ (cm}^3 \text{ mol}^{-1}) = 87.621 - 0.560m_b \quad (\text{S.D.} = 0.019) \quad (6)$$

where S.D. is the abbreviation of standard deviation. The molar enthalpy of solution of butanamide in pure water, 9083 J mol^{-1}, agrees very well with 9070 J mol^{-1} reported in [10] and 9075 J mol^{-1} reported in [11]. The standard partial molar volume of butanamide, 87.621 cm^3 mol^{-1}, agrees very well with 87.1 cm^3 mol^{-1} reported in [12]. The transfer enthalpies and standard transfer volumes of butanamide from pure water to aqueous alkan-1-ol solutions have been calculated and fitted, respectively, to Eqs. (2) and (6) by using a least-squares method. The enthalpic interaction coefficients are given in Table 1 and volumetric interaction coefficients in Table 2.

4.1. Pair interaction

Seen from Table 1, h_{ab} have positive values, and increase with increasing size of the apolar chain of alkan-1-ol molecules. Also shown in Table 2, V_{ab} are negative varying from small to large values with the hydrocarbon chain extent. These are consistent with the interactions between formamide and alkan-1-ols [5].

The solute–solute interaction coefficients are related to the variations of thermodynamic properties when two solvated solute particles are brought from an infinite distance to a finite one where their hydration shells are perturbed [13]. As for the polar non-electrolyte molecules with alkyl groups, the overall effects among the solutes reflect the following three effects [14]: (1) dipole–dipole interaction between polar groups, (2) hydrophobic–hydrophobic interaction of the alkyl groups, (3) 'thermochemical repulsion' between the solvated apolar alkyl groups and solvated polar groups. The first effect is exothermic and is accompanied by partial desolvation of polar groups, which is an endothermic effect, thus weakening the exothermic effect caused by the dipole–dipole interaction. According to the destructive overlap model [15], the partial desolvation of polar

Table 2
The volumetric interaction coefficients of butanamide in aqueous alkan-1-ol solutions at 298.15 K

Alkan-1-ol	V_{ab} (cm^3 kg mol^{-2})	V_{abb} (cm^3 kg^2 mol^{-3})	V_{aab} (cm^3 kg^2 mol^{-3})
Methanol	−0.361 ± 0.002	0.027 ± 0.001	0.044 ± 0.003
Ethanol	−0.690 ± 0.007	0.071 ± 0.003	0.118 ± 0.008
Propanol	−0.911 ± 0.007	0.182 ± 0.003	0.151 ± 0.008

±n is the S.E.

groups will make some of the previously electrostricted water molecules return to their normal structure, causing a positive value to V_{ab}. On the other hand, the 'thermochemical repulsion' will make some water molecules in the hydrophobic hydration shell return to the bulk. Because the density of water is lower than that in bulk [16,17], the effect will produce a positive contribution to h_{ab} and a negative contribution to V_{ab}. As for formamide–alcohol interaction in water, because formamide has no alkyl groups, they will associate in head-on fashion and only dipole–dipole interaction and the 'thermochemical repulsion' are taken into account [5]. Whereas, for the system in this study when alkan-1-ols with alkyl groups interact with butanamide, they will associate in the side-by-side manner [18]. Apart from dipole–dipole interaction and the 'thermochemical repulsion', there also exist hydrophobic–hydrophobic groups overlapping each other. In this process, more water molecules are squeezed out of the hydrophobic hydration shell to the bulk. Therefore, the effect will cause a larger positive contribution to h_{ab}, and larger negative contribution to V_{ab}. With the alkyl chain extended, the hydrophobic–hydrophobic interaction becomes more and more pronounced. Consequently, for butanamide interacting with alkan-1-ol molecules, positive h_{ab} increase from methanol, ethanol to propanol, and negative V_{ab} decrease in values.

4.2. Triplet interaction

As shown in Tables 1 and 2, the enthalpic and volumetric triplet interaction coefficients for all ternary systems are all positive and much smaller in value than the pair interaction coefficients. In addition, the triplet interaction coefficients increase with the alkyl chain extent. Suppose that another molecule participate in the triplet interaction in the similar way to the two overlapping co-region molecules, the triplet coefficients, whether enthalpic or volumetric interaction coefficients would be the same sign with the corresponding pair interaction coefficients and furthermore, present larger values. This is, obviously, inconsistent with the experimental data. These evidences indicate that the triplet interaction and the pair interaction of the interacting molecules are different in the interaction mechanism.

The a–b–b type triplet interaction includes the interaction among two butanamide molecules and one alkan-1-ol molecule. The a–a–b type triplet interaction includes the interaction among one butanamide molecule and two alkan-1-ol molecules. Franks [19] has pointed out that there is solvent separated association among hydrophobic solutes. In a Monte Carlo simulation study [20], some evidences were found for the coexistence of solvent separated and direct contact configurations. We think that no dipole–dipole interaction occurs in the triplet interaction between the third molecule and the pair of two molecules associated in side-by-side manner, and their alkyl groups will take place the solvent separated association. The direct contact among alkyl groups are hydrophobic–hydrophobic interaction, mentioned often, which will break the hydrophobic hydration structure of the alkyl groups. But the solvent separated association will not have the same effect. Molecular dynamics simulations have obtained that the hydrophobic group has a blocking effect [16] or a protecting effect [17] for the hydra-

tion shell water molecules. The two effects have been ascribed to a shielding effect [11]. Hydrophobic group can shield its hydrophobic hydration structure from the shock of other water molecules. For the kind of solvent separated association, aside from the shielding effect of the hydrophobic groups themselves, with no co-region overlap occurring, they will provide a mutual shielding effect among the associated hydrophobic groups. This means that the solvent separated association not only does not break the hydrophobic hydration structure of the alkyl groups but also increase the structure with the mutual shielding effect, which is contrary to the direct contact association. As a result, the solvent separated association will cause a negative contribution to enthalpic functions and positive to volumetric coefficients. The triplet interaction mechanism could explain why the triplet volumetric interaction coefficients are opposite in sign and why the triplet enthalpic interaction coefficients are smaller in value to the corresponding pair coefficients.

Interestingly, for butanamide in this study, the homotactic enthalpic interaction coefficient (h_{bb}) is positive (615 J kg mol^{-1}) and homotactic volumetric interaction coefficient (V_{bb}) is negative (-0.560 cm^3 kg mol^{-2}). The large, positive homotactic interaction coefficient indicates a typical behavior of prevailingly hydrophobic solutes [21]. Whereas, for formamide, opposite results have been revealed in [5]. The homotactic enthalpic interaction coefficient (h_{bb}) for formamide is negative (-134 J kg mol^{-1}) and homotactic volumetric interaction coefficient (V_{bb}) is positive (0.104 cm^3 kg mol^{-2}). Just as Lilley and co-workers [18] have proposed, as for polar molecules with longer alkyl chains, two molecules associate in side-by-side manner and the homotactic enthalpic pair interaction coefficient (h_{bb}) is generally positive and the homotactic volumetric pair interaction coefficient (V_{bb}) is generally negative. Whereas, as for polar molecules with shorter or no alkyl chains, two molecules associate in head-on fashion and h_{bb} is generally negative and V_{bb} is generally positive. That is why h_{bb} for butanamide is positive (615 J kg mol^{-1}) and V_{bb} is negative (-0.560 cm^3 kg mol^{-2}). Whereas, for formamide, opposite results have been revealed.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.07.002.

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