Thermochimica Acta 386 (2002) 103–110

thermochimica acta

www.elsevier.com/locate/tca

Calorimetric and volumetric studies of the interactions of butyramide in aqueous carboxylic acid solutions at 298.15 K

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Received 8 May 2001; received in revised form 14 September 2001; accepted 25 September 2001

Abstract

Enthalpies of solution and apparent molar volumes have been determined for butyramide in aqueous formic acid, acetic acid and propionic acid solutions using a C-80 microcalorimeter and vibrating tube digital densimeter. From the data, enthalpic and volumetric interaction coefficients were obtained. The pair interaction coefficients are discussed from the point of view of dipole–dipole and structural interactions and we have also tried to interpret the triplet interaction coefficients according to the solvent separated association pattern. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Butyramide; Carboxylic acid; Apparent volume; Enthalpy of solution; Interaction coefficients

1. Introduction

As is well known, the basis of life is protein. In solution and biological chemistry, it is very important to study the interaction between groups which exist in proteins. Model systems of polypeptides, amide + carboxylic acid mixtures, play a very important role in regulating the order⇌disorder transformation reaction, which exists inter- and intramolecularly of proteins because they could give much information about solute–solute and long range intramolecular interactions [1,2]. Such systems have been investigated by a variety of physiochemical techniques such as infrared, NMR, viscosity, conductance and mass spectra, etc. [3–5].

However, systems, amide + carboxylic acid + water, have never been found in the literature by measuring density and calorimeter. The present work reports the apparent molar volumes and enthalpies of solution of butyramide in carboxylic acid + water mixtures, intending on covering the gap in the literature and giving an indirect contribution to the understanding of the complicated behavior of proteins in various mixed mediums.

2. Experimental section

2.1. Materials

Butyramide, formic acid, acetic acid and propionic acid were purified by the standard methods described in the literature [6]. Analytical reagent grade butyramide was recrystallized twice from ethanol + water mixtures and dried under vacuum for 10 h, thereafter, stored over P_2O_5 in a desiccator prior to use. Formic acid (AR) was kept over *o*-phthalic anhydride for 6 h and then distilled. To remove the last trances of water, formic acid was stirred with boric anhydride for at

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PII: S0040-6031(01)00810-3

least 48 h and fractionally distilled under a reduced pressure at 298.15 K. Acetic acid (AR) was washed with a calculated amount of acetic anhydride for about 10 h and fractionally distilled. Finally, acetic acid was stirred with potassium permanganate for 5 h and fractionally distilled. Propionic acid (AR) was dried over anhydrous sodium sulfate for about 24 h and then distilled. Finally, it was fractionally distilled over potassium permanganate and the middle fraction distilling at 413.15–414.15 K was collected. All the acids were stored in sealable bottles and dried over P_2O_5 prior to use. Water of conductivity 1.2×10^{-4} S m^{-1} was obtained by distilling deionized water from alkaline $KMnO_4$ to remove any organic matter. All solutions were prepared freshly by weighing on the molality scale.

2.2. Apparatus and measurements

The enthalpies of solution were measured at 298.15 K using a C-80 calorimeter (Setaram) using reversed-mixing vessels. The reversed-mixing vessel has two chambers separated by a tilting lid. About 0.04–0.3 g of butyramide was introduced into the vessel, then the lid was put in place. The butyramide was weighed on a single-pan balance (Mettler) with a sensitivity of 10 μg. In order to obtain a complete separation of the chambers, 0.5 g of mercury was put into the vessel before the solvent was introduced. About 5 ml solvent was weighed on an analytical balance with a sensitivity of 0.1 mg and introduced into the vessel. The calibration of the calorimeter was performed with an EJ2 Joule-effect device (Setaram). The total uncertainty in the enthalpy of solution was about ±0.5%.

Solution densities were measured at 298.15 K with a vibrating-tube digital density meter (model 60/602, Anton Paar) which has been described carefully in [7]. The precision of the density meter is $\pm1.5\times10^{-6}$ g cm^{-3}. The temperature around the density meter cell was controlled by circulating water from a constant-temperature bath (Schott, Germany). A CT1450 temperature controller and a CK-100 ultracryostat were employed to maintain the temperature at 298.15 ± 0.005 K. The density meter was calibrated with the known densities of dry air and conductivity water daily. The density of pure water at 298.15 K was taken as 0.99705g cm^{-3} [8]. Reproducibility of the density measurements was better than $\pm3\times10^{-6}$ g cm^{-3}.

3. Results

The measured enthalpies of solution of butyramide in water and in various carboxylic acid solutions are, respectively, given in Tables 1–4. According to the McMillan and Mayer approach [9], all the thermodynamic properties of multi-component solutions can be expressed by using a viral expansion in m 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 butyramide (b) from pure water (w)

Table 1
The enthalpies (J mol^{-1}) of solution H_m of butyramide in pure water at 298.15 K

m_b (mol kg^{-1})	H_m	m_b (mol kg^{-1})	H_m
0.1169	9163	0.3960	9326
0.1865	9182	0.4595	9374
0.2538	9225	0.5374	9389
0.3260	9257	0.6037	9456

Table 2
The enthalpies (J mol^{-1}) of solution H_m of butyramide in formic acid solutions at 298.15 K

m_b (mol kg^{-1})	H_m (m_a = 0.5000)	m_b (mol kg^{-1})	H_m (m_a = 1.0000)	m_b (mol kg^{-1})	H_m (m_a = 2.0000)	m_b (mol kg^{-1})	H_m (m_a = 3.0001)
0.1244	9632	0.1240	10132	0.1250	10857	0.1297	11504
0.2130	9685	0.2219	10184	0.2262	10904	0.2339	11559
0.3135	9741	0.3190	10223	0.3327	10978	0.3426	11603
0.4108	9794	0.4128	10276	0.4299	11035	0.4449	11644
0.5020	9843	0.5130	10313	0.5218	11054	0.5352	11688
0.6072	9906	0.6076	10385	0.6295	11112	0.6465	11736

Table 3
The enthalpies (J mol^{-1}) of solution H_m of butyramide in acetic acid solutions at 298.15 K

m_b (mol kg^{-1})	H_m (m_a = 0.5000)	m_b (mol kg^{-1})	H_m (m_a = 1.0000)	m_b (mol kg^{-1})	H_m (m_a = 2.0001)	m_b (mol kg^{-1})	H_m (m_a = 3.0000)
0.1246	9801	0.1397	10349	0.1346	11328	0.1397	12131
0.2241	9848	0.2289	10395	0.2370	11382	0.2463	12182
0.3197	9898	0.3176	10447	0.3402	11433	0.3542	12249
0.4123	9953	0.4209	10510	0.4535	11495	0.4643	12303
0.5177	10013	0.5231	10566	0.5492	11547	0.5714	12336
0.6056	10064	0.6275	10622	0.6592	11607	0.6945	12398

Table 4
The enthalpies (J mol^{-1}) of solution H_m of butyramide in propionic acid solutions at 298.15 K

m_b (mol kg^{-1})	H_m (m_a = 0.5000)	m_b (mol kg^{-1})	H_m (m_a = 0.9999)	m_b (mol kg^{-1})	H_m (m_a = 2.0000)	m_b (mol kg^{-1})	H_m (m_a = 3.0002)
0.1248	9959	0.1266	10703	0.1321	12112	0.1428	13034
0.2224	10027	0.2250	10754	0.2436	12162	0.2596	13069
0.3257	10079	0.3315	10812	0.3379	12191	0.3677	13130
0.4253	10136	0.4266	10863	0.4621	12264	0.4869	13192
0.5146	10186	0.5341	10923	0.5656	12323	0.5930	13233
0.6100	10253	0.6357	11002	0.6642	12371	0.7061	13272

to carboxylic acid (a) aqueous solutions can be expressed as mentioned in [10]

$$\Delta_{tr}H_b(\mathrm{w} \rightarrow \mathrm{w}+\mathrm{a}) = 2h_{ab}m_a + 3h_{abb}m_am_b + 3h_{aab}m_a^2 + \cdots \quad (1)$$

where m_a and m_b are the molalities defined per kilogram of pure water, h_{ab} is the heteroactic enthalpic pair interaction coefficient, h_{abb} and h_{aab} are the enthalpic triplet interaction coefficients. For the system studied, we used the truncated form of the equation as [11]

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

The molar enthalpies of butyramide in pure water is found to be a very linear function of the amide molality over the molality range studied and can be expressed by the following equation:

$$\Delta H_m(\mathrm{J\,mol^{-1}}) = 9075 + 615m_b \quad (3)$$

The limiting molar enthalpy of solution in Eq. (3) agrees very well with the literature [12] value of 9070 J mol^{-1}. The homoactic enthalpic interaction coefficient (h_{bb}) is 615 J kg mol^{-1} shown as above. The large, positive homoactic interaction coefficient indicates a typical behavior of prevailingly hydrophobic solutes [13]. The transfer enthalpies of butyramide from pure water to the aqueous solutions of three carboxylic acids have been calculated and fitted to Eq. (2) using a least squares method and the enthalpic interaction coefficients thus obtained, are given in Table 5.

Densities, at 298.15 K, of solutions of butyramide in water and in three carboxylic acid aqueous solutions are, respectively, given in Tables 6–9. The density data are used to calculate the apparent molar volumes of butyramide using

$$\Phi_{V_b} = \frac{M_b}{\rho} - \frac{10^3(\rho - \rho_0)}{m'_b}\rho\rho_0 \quad (4)$$

Table 5
The enthalpic interaction coefficients of butyramide with some carboxylic acids in aqueous solutions at 298.15 K

Carboxylic acid	h_{ab} (J kg mol^{-2})	h_{abb} (J kg^2 mol^{-3})	h_{aab} (J kg^2 mol^{-3})
Formic acid	513 ± 6	−28 ± 8	−25 ± 1
Acetic acid	660 ± 4	−21 ± 5	−36 ± 1
Propionic acid	847 ± 7	−18 ± 9	−42 ± 2

Table 6
Densities and apparent molar volumes of butyramide in pure water at 298.15 K

m_b (mol kg^{-1})	ρ (g cm^{-3})	Φ_{V_b} (cm^3 mol^{-1})
0.20150	0.997019	87.535
0.31223	0.997028	87.450
0.41058	0.997052	87.373
0.50527	0.997083	87.310
0.62795	0.997117	87.265
0.71314	0.997160	87.213
0.82703	0.997210	87.169
0.92042	0.997269	87.119

Table 7
Densities and apparent molar volumes of butyramide in aqueous formic acid solutions at 298.15 K

m_a (mol kg^{-1})	m_b (mol kg^{-1})	ρ (g cm^{-3})	Φ_{V_b} (cm^3 mol^{-1})
0.50447	0.00000	1.002537	
	0.18060	1.002390	87.741
	0.30745	1.002315	87.654
	0.41420	1.002268	87.584
	0.51478	1.002235	87.523
	0.61758	1.002207	87.472
	0.70654	1.002191	87.428
	0.82485	1.002172	87.382
	0.92054	1.002159	87.351
0.99260	0.00000	1.007573	
	0.20643	1.007288	87.912
	0.30386	1.007174	87.853
	0.39612	1.007081	87.787
	0.50302	1.006976	87.740
	0.60580	1.006903	87.663
	0.70549	1.006818	87.633
	0.79689	1.006755	87.594
	0.95968	1.006648	87.538
1.51211	0.00000	1.012589	
	0.20536	1.012197	88.062
	0.30304	1.012029	88.013
	0.39758	1.011868	87.991
	0.50556	1.011702	87.944
	0.59870	1.011577	87.888
	0.71890	1.011420	87.835
	0.81236	1.011295	87.811
	0.95512	1.011094	87.799
2.00476	0.00000	1.017138	
	0.19517	1.016673	87.208
	0.28297	1.016484	87.149
	0.38049	1.016269	87.139
	0.48719	1.016072	87.054
	0.58412	1.015857	87.078
	0.68724	1.015645	87.075
	0.77978	1.015501	87.010
	0.98524	1.015130	86.978

Table 8
Densities and apparent molar volumes of butyramide in aqueous acetic acid solutions at 298.15 K

m_a (mol kg^{-1})	m_b (mol kg^{-1})	ρ (g cm^{-3})	Φ_{V_b} (cm^3 mol^{-1})
0.49970	0.00000	1.001075	
	0.20255	1.000981	87.512
	0.29933	1.000953	87.456
	0.38023	1.000935	87.417
	0.51494	1.000919	87.351
	0.61931	1.000916	87.304
	0.72141	1.000916	87.267
	0.80010	1.000919	87.241
	0.88643	1.000923	87.216
0.99994	0.00000	1.004839	
	0.19582	1.004684	87.545
	0.30201	1.004609	87.520
	0.40418	1.004553	87.468
	0.49423	1.004505	87.439
	0.60261	1.004458	87.398
	0.69685	1.004420	87.368
	0.80640	1.004381	87.337
	0.90783	1.004345	87.315
1.49949	0.00000	1.008325	
	0.20113	1.008106	87.587
	0.30734	1.008000	87.563
	0.39604	1.007910	87.560
	0.55407	1.007769	87.525
	0.71197	1.007642	87.489
	0.80703	1.007569	87.471
	0.92910	1.007476	87.454
2.00109	0.00000	1.011613	
	0.20306	1.011333	87.654
	0.30675	1.011194	87.651
	0.40952	1.011060	87.646
	0.49468	1.010951	87.642
	0.61800	1.010795	87.640
	0.70138	1.010701	87.622
	0.79965	1.010580	87.623
	0.89816	1.010469	87.613

where M_b is the molecular weight of butyramide. If Eq. (4) is used in butyramide + water binary systems, m'_b is the molality, ρ and ρ_0 are, respectively, the densities of the solutions and water. If used in butyramide + carboxylic acid +water ternary systems, m'_b should be calculated on the basis of the mass of carboxylic acid and water, ρ is the density of the ternary systems, and ρ_0 is the density of carboxylic acid + water binary solution. In the present work, to get the same scale with enthalpy data, m_b, which is the molality defined per kilogram of pure water, can be used to take the place of m'_b. The relationship between

Table 9
Densities and apparent molar volumes of butyramide in aqueous propionic acid solutions at 298.15 K

m_a (mol kg^{-1})	m_b (mol kg^{-1})	ρ (g cm^{-3})	Φ_{V_b} (cm^3 mol^{-1})
0.49980	0.00000	1.000129	
	0.19404	1.000079	87.381
	0.29575	1.000068	87.328
	0.40896	1.000065	87.277
	0.50554	1.000074	87.226
	0.59664	1.000087	87.185
	0.68968	1.000096	87.161
	0.80841	1.000110	87.135
	0.88953	1.000123	87.116
1.00080	0.00000	1.002923	
	0.20427	1.002840	87.307
	0.30109	1.002814	87.262
	0.39885	1.002783	87.253
	0.51676	1.002744	87.252
	0.58618	1.002727	87.240
	0.69462	1.002692	87.241
	0.83136	1.002673	87.209
	0.89862	1.002654	87.209
1.50191	0.00000	1.005461	
	0.20416	1.005323	87.401
	0.29690	1.005264	87.393
	0.39151	1.005203	87.394
	0.51035	1.005125	87.400
	0.57359	1.005079	87.412
	0.71894	1.004998	87.395
	0.82684	1.004936	87.390
	0.87644	1.004904	87.394
1.99963	0.00000	1.007723	
	0.20110	1.007526	87.577
	0.30077	1.007431	87.576
	0.40439	1.007323	87.605
	0.49964	1.007236	87.597
	0.60312	1.007120	87.635
	0.70518	1.007017	87.646
	0.80294	1.006941	87.622
	0.88734	1.006846	87.646

m_b and m'_b is as follows:

$$m'_b = \frac{10^3 m_b}{(1000 + m_a M_a)} \tag{5}$$

Therefore, the apparent molar volumes of butyramide are also calculated using

$$\Phi_{V_b} = \frac{(1000 + m_a M_a + m_b M_b)}{m_b \rho} - \frac{(1000 + m_a M_a)}{m_b \rho_0} \tag{6}$$

where M_a is the molecular weight of carboxylic acids. Calculated apparent molar volumes of butyramide in water and in aqueous carboxylic acid solutions are also listed in Tables 6–9. According to the McMillan and Mayer approach [10], just the same as the transfer enthalpy in Eq. (1), the standard transfer volumes of butyramide from pure water to aqueous carboxylic acid solutions, can be expressed as follows:

$$\Delta_{tr}\Phi_{V_b}(w \rightarrow w + a) = 2V_{ab}m_a + 3V_{abb}m_a m_b + 3V_{aab}m_a^2 + \cdots \tag{7}$$

We also use the truncated form as

$$\frac{\Delta_{tr}\Phi_{V_b}(w \rightarrow w + a)}{m_a} = 2V_{ab} + 3V_{abb}m_b + 3V_{aab}m_a \tag{8}$$

where V_{ab} is the heteroactic volumetric pair interaction coefficient, V_{abb} and V_{aab} are the volumetric triplet interaction coefficients. The apparent molar volumes listed in Tables 6–9 have been fitted to Eq. (8) using a least squares method and the volumetric interaction coefficients, thus obtained, are given in Table 10.

4. Discussion

4.1. Pair interaction

The physical meaning of the solute–solute interaction coefficients is, generally, linked to the variations

Table 10
The volumetric interaction coefficients of butyramide with some carboxylic acids in aqueous solutions at 298.15 K

Carboxylic acid	V_{ab} (cm^3 kg mol^{-2})	V_{abb} (cm^3 kg^2 mol^{-3})	V_{aab} (cm^3 kg^2 mol^{-3})
Formic acid	0.188 ± 0.004	0.032 ± 0.003	−0.007 ± 0.001
Acetic acid	−0.047 ± 0.003	0.085 ± 0.003	0.020 ± 0.001
Propionic acid	−0.245 ± 0.005	0.128 ± 0.004	0.073 ± 0.002

of thermodynamic properties when two solvated solute particles are brought from an infinite instance to a finite where their hydration shells are perturbed [14]. Generally speaking, the interaction is composed of electrostatic and structural interaction [15]. As is known, butyramide is a polar molecule, and carboxylic acid exists partly in a disassociated state in solutions. For the systems discussed here, in the range of the concentration adopted here, the ionization constant [16] indicates that only 1.9 of solute molecules are ionized in an aqueous solution of formic acid ($m = 0.5\ \mathrm{mol\ kg^{-1}}$) at 298.15 K. Compared to other acids, formic acid is a more acidic acid, so ion concentration for the other carboxylic acids is lower than that of the formic acid systems. Therefore, the contribution of ionic species to the solution structure can be disregarded here.

As for the polar non-electrolyte molecules with alkyl groups, the overall effects among the solutes reflect the following three effects [17], (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 latter two effects are related to the hydrophobic hydration. The 'iceberg formation' model proposed by Frank and Evans [18] has stated that the structure of water is strengthened around hydrophobic solutes, which has also been examined and confirmed both experimentally and theoretically [19]. Investigations indicated that the structure-strengthening of water around hydrophobic groups is associated with the local density decreasing around them [19,20].

Seen from Table 5, h_{ab} have positive values and increase with increasing size of the apolar side chain of carboxylic acids. Also shown in Table 10, for formic acid, V_{ab} are positive, but in acetic acid or propionic acid solutions, V_{ab} are negative varying from small to large values with the hydrocarbon chain extended. Without alkyl chain, formic acid belongs to a strong polar molecule. The interaction between formic acid and butyramide can be considered comprised of the two terms, the direct interaction of dipole–dipole groups (exothermic effect) and the 'thermochemical repulsion' between carboxyl groups and the apolar chain of butyramide. The dipole–dipole interaction is accompanied by partial desolvation of them, which is an endothermic effect, thus weakening the exothermic effect caused by the dipole–dipole interaction. In the meanwhile, the 'thermochemical repulsion' breaks the hydrophobic hydration structure of the alkyl groups, thus causing a positive contribution to h_{ab}. According to the destructive overlap model [21,22], when the interactions between dipolar–dipolar groups occur, some of the previously electrostricted water molecules will 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 in the hydrophobic hydration is lower than that in bulk, the effect will produce a negative contribution to V_{ab}. The experiment data indicate the former effect is prevailing.

Gallardo et al. [23] have proposed that two amino acid molecules with the alkyl groups associate in solutions in a side-by-side manner. Based on the experimental data, the interaction of one butyramide molecule and one acetic or propionic acid molecule also abides by the side-by-side manner. In contrast with the interaction of butyramide and formic acid, when butyramide associates with acetic or propionic acid according to the side-by-side manner, there also exist hydrophobic–hydrophobic groups overlapping each other, apart from dipole–dipole interaction and the 'thermochemical repulsion'. In this process, some water molecules are squeezed out of the hydrophobic hydration shell to the bulk, therefore, the effect will cause a positive contribution to h_{ab} and a negative value to V_{ab} because the hydrogen bonds in co-region are stronger than in bulk. With the alkyl chain extended, hydrophobic–hydrophobic interaction becomes more and more pronounced, causing h_{ab} increase and V_{ab} variation from positive to negative.

4.2. Triplet interaction between butyramide and acetic acid or propionic acid in solutions

There exist two sets of triplet interaction coefficients. One is h_{abb} and V_{abb}, which represent the enthalpic and volumetric interactions of two butyramide molecules and one carboxylic acid molecule; the other is h_{aab} and V_{aab}, which relate to the triplet interactions between two carboxylic acid molecules and one butyramide molecule. As shown in Table 5, the heteroactic pair interaction coefficients, h_{ab}, are presented to be positive for all ternary systems. According to the literature [24], the homoactic pair interaction coefficients, h_{aa}, of three various carboxylic acids are all positive. In the meantime, the homoactic pair interaction coefficient (h_{bb}) of butyramide is also positive just as mentioned above. In contrast to the positive values of the pair interaction coefficients, all enthalpic triplet interaction coefficients, h_{abb} and h_{aab}, are found to be negative from Table 5. In addition, we can also see from Table 10 that the triplet volumetric interaction coefficients for all ternary systems, except formic acid, are opposite in sign to the corresponding pair interaction coefficients, which is a general behavior of many hydrophobic solutes such as TBA, BU_tNBr and triethylamine [22]. When three polar non-electrolyte molecules with alkyl groups interact in solutions, two molecules first associate in a side-by-side manner [23]. Given another molecule participates in the triplet interaction in similar way to the two overlapping co-region molecules, the triplet coefficients, whether enthalpic or volumetric, 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.

In the association of side-by-side manner of two molecules, there is stronger dipole–dipole interaction between their polar groups, which will make their alkyl chains direct contact. The direct contact breaks the hydrophobic hydration structure of the overlapping co-region. Franks [25] has pointed out that there is solvent separated association among hydrophobic solutes. In a Monte Carlo simulation study [26], 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 solvent separated association. The molecular dynamics calculations have obtained that the hydrophobic group has a protecting effect [20] or a blocking effect [19] for the hydration shell water molecules. We can ascribe the two effects to a shielding effect. 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 is to say 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 value to enthalpic functions and positive to volumetric coefficients. This is why the triplet enthalpic and volumetric interaction coefficients are opposite in sign to the corresponding pair coefficients.

4.3. Triplet interaction between butyramide and formic acid in solutions

Compared to acetic acid or propionic acid, no alkyl chain exists in formic acid. As a result, the triplet interaction between formic acid and butyramide is largely different from that of acetic acid or propionic acid and butyramide, which has also been manifested in our experimental data. Seen from Tables 5 and 10, the triplet enthalpic coefficients, for formic acid, whether h_{abb} or h_{aab}, are smaller than h_{ab}, which is very consistent with acetic acid or propionic acid. But, the triplet volumetric functions, V_{ab} and V_{aab}, are smaller than V_{av}, obviously contrary to those of acetic acid or propionic acid and butyramide molecules. With no alkyl chain, when two formic acid molecules interact with one butyramide molecule in solutions, the solvent separated association will not occur. As for two butyramide molecules interacting with one formic acid molecule, the solvent separated association effect may happen, but it is obviously invalid to try to interpret the experimental data in view of the triplet interaction pattern mentioned above. In present work, we can not give a reasonable explanation to the triplet interaction between formic acid and butyramide molecules, and further investigation is required to interpret it.

Acknowledgements

This project 29773011 is supported by the National Natural Science Foundation of China. The authors are much grateful to this foundation for financial support.

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