Thermochimica Acta, 214 (1993) 195–201
Elsevier Science Publishers B.V., Amsterdam

Thermochemical studies on water–butane-1,2-diol–NaI and water–butane-1,4-diol–NaI at 298.15 K

Jadwiga Woźnicka [a] and Adam Bald [b]

[a] *Department of Physical Chemistry, University of Łódź, Pomorska 18, 91-416 Łódź (Poland)*

[b] *Department of Chemical Didactics, University of Łódź, Lindleya 3, 90-136 Łódź (Poland)*

(Received 4 May 1992)

Abstract

Measurements of the dissolution enthalpies of NaI in water–butane-1,2-diol and water–butane-1,4-diol mixtures have been carried out using an "isoperibol" type calorimeter at 298.15 K. The course of the standard enthalpy of solution $\Delta H_m^\ominus$, vs. the binary solvent composition has been discussed.

INTRODUCTION

Polyalcohols, their mixtures with water or organic solvents and electrolytes in these mixtures have been investigated in our laboratories for several years [1–3]. Recently, a growing interest in aqueous solutions of polyhydroxy compounds can be observed, mostly due to their numerous uses in research into biochemical processes [4, 5]. The literature on such systems is, however, rather incomplete.

Our previous reports included the results of densimetric, viscosimetric and dielectric measurements of water–butane-1,4-diol (BD-1,4) [6] and water–butane-1,2-diol (BD-1,2) [7] systems. The conductivity of NaI in these mixtures has also been measured and interpreted. The studies on isomeric butanediols were aimed at evaluating the effect of the hydroxy group positions in diol molecules on the mixture properties.

It was to be expected that the longer the alkyl free radical in the diol molecule, the higher the probability of hydrophobic interactions in aqueous solutions. Considering the considerable differences in permittivity values between both diols ($\varepsilon_{BD\text{-}1,2} = 22.7$, $\varepsilon_{BD\text{-}1,4} = 30.3$) and water ($\varepsilon_{H_2O} = 78$), one should expect ionic pairs to be present in diol-rich solutions.

Correspondence to: A. Bald, Department of Chemical Didactics, University of Łódź, Lindleya 3, 90-136 Łódź, Poland.

The present paper describes the results of our studies on the enthalpy of solution of NaI in water–BD-1,2 and water–BD-1,4 systems at $T = 298.15$ K.

EXPERIMENTAL

Water, BD-1,2, BD-1,4, and sodium iodide were prepared as described previously [6, 7]. Measurements of the enthalpy of NaI solution were carried out using an "isoperibol" type calorimeter [1]. The error involved in the measurements was estimated to be ±0.5%.

RESULTS AND DISCUSSION

Enthalpies of solution of NaI in water–BD-1,2 and water–BD-1,4 systems were measured over the entire range of mixed solvent compositions at 298.15 K. The salt concentration was within the range of about 0.002–0.02 mol kg^{-1} of solvent. The dissolution of NaI in all the water–butanediol mixtures is exothermic (Tables 1 and 2).

The values of the enthalpy of solution (ΔH_m) along with those of density (ρ_0) and relative permittivity (ε) previously obtained for the water–BD-1,2 [6] and water–BD-1,4 [7] systems were used to calculate the standard enthalpy of solution ($\Delta H_m^{\ominus}$) by the method of Criss and Cobble [8]. The results obtained are given in Table 3. As is seen from Fig. 1, the function $\Delta H_m^{\ominus} = f$(mol.% diol) shows an endothermic maximum at about 5 mol.% BD-1,2 and 10 mol.% BD-1,4 in water.

Similar maxima have been observed previously in aqueous-alcoholic solutions of electrolytes [9]. Krestov et al. [10] have reported the endothermic maximum of the enthalpies of solution of LiCl, NaCl and KCl in mixtures of water with propane-1,2-diol and BD-1,4. These authors explain this fact in terms of stabilization of the solution structure by hydrophobic interactions between water and alkyl radicals of alcohols and diols. This is also our view.

Our results, however, point to different behaviour by BD-1,2 and BD-1,4. In water–BD-12 solution, the maximum appears at lower diol content than that in water–BD-1,4 systems. It can be concluded that a lower BD-1,2 quantity is sufficient to bring about the maximum stabilization of the solution structure. This seems to be reasonable because "exposed" alkyl radicals ($\cdot CH_3$) are present in BD-1,2, facilitating interactions with water.

Having the conductometric data of water–BD-1,2–NaI and water–BD-1,4–NaI systems previously obtained [6, 7], we could "correct" the values of $\Delta H_m^{\ominus}$. One can expect that the ionic association will take place in diol-rich solutions, especially in BD-1,2. The ionic association constant in pure BD-1,4 is about 12 and in BD-1,2 about 50.

TABLE 1

Enthalpies of solution of NaI in water–BD-1,4 mixtures at 298.15 K

m_{NaI} (mol kg^{-1})	$-\Delta H_{\mathrm{m}}$ (kJ mol^{-1})	m_{NaI} (mol kg^{-1})	$-\Delta H_{\mathrm{m}}$ (kJ mol^{-1})	m_{NaI} (mol kg^{-1})	$-\Delta H_{\mathrm{m}}$ (kJ mol^{-1})
Water		*20 mol% BD-1,4*		*80 mol. % BD-1,4*	
0.00345	7.50	0.00480	6.61	0.00108	22.76
0.00660	7.52	0.00702	6.57	0.00191	22.59
0.00932	7.52	0.01164	6.54	0.00349	22.43
0.01274	7.53	0.01173	6.54	0.00415	22.34
0.01728	7.54	0.02260	6.53	0.01030	21.84
0.02040	7.57	0.02532	6.51	0.01525	21.51
2 mol. % BD-1,4		*30 mol. % BD-1,4*		*90 mol. % BD-1,4*	
0.00492	6.86	0.00433	9.67	0.00118	24.98
0.00493	6.86	0.00886	9.50	0.00195	24.81
0.01042	6.88	0.00984	9.50	0.00460	24.48
0.01164	6.88	0.01445	9.41	0.00899	24.06
0.01351	6.88	0.01909	9.37	0.01573	23.56
0.01697	6.90	0.02718	9.25	0.02201	23.14
5 mol. % BD-1,4		*50 mol. % BD-1,4*		*95 mol. BD-1,4*	
0.00599	6.37	0.00155	15.31	0.00202	25.71
0.00626	6.38	0.00478	15.10	0.00349	25.44
0.01070	6.36	0.00565	15.02	0.00619	25.08
0.01110	6.33	0.01251	14.73	0.00933	24.77
0.01823	6.34	0.01772	14.64	0.01251	24.56
0.02679	6.32	0.02271	14.48	0.01557	24.31
10 mol. % BD-1,4		*70 mol. BD-1,4*		*100 mol. % BD-1,4*	
0.00538	6.20	0.00280	20.17	0.00479	25.98
0.00898	6.15	0.00571	19.87	0.00522	25.90
0.00975	6.14	0.00645	19.79	0.00886	25.48
0.01218	6.11	0.01129	19.54	0.01051	25.27
0.01692	6.07	0.01553	19.41	0.01607	24.64
0.01707	6.07	0.01982	19.20	0.02376	24.10

To correct the value of $\Delta H_{\mathrm{m}}^{\ominus}$ we used the method of calculation in the model presented in ref. 11 by Barthel et al. According to this method the relative apparent molal content of solution containing "free ions" (FIs) and ion pairs is presented as a sum

$$\Phi_{\mathrm{L}} = \alpha\Phi_{\mathrm{L}}(\mathrm{FI}) + (1-\alpha)\,\Delta H_{\mathrm{A}}^{\ominus} \qquad (1)$$

where $\Phi_{\mathrm{L}}(\mathrm{FI})$ is the relative apparent molal heat content of the solution with the "free ions", $\Delta H_{\mathrm{A}}^{\ominus}$ denotes the enthalpy of ion pair formation and

TABLE 2

Enthalpies of solution of NaI in water–BD-1,2 mixtures at 298.15 K

m_{NaI} (mol kg^{-1})	$-\Delta H_{\mathrm{m}}$ (kJ mol^{-1})	m_{NaI} (mol kg^{-1})	$-\Delta H_{\mathrm{m}}$ (kJ mol^{-1})	m_{NaI} (mol kg^{-1})	$-\Delta H_{\mathrm{m}}$ (kJ mol^{-1})
Water		*20 mol. % BD-1,2*		*80 mol. % BD-1,2*	
0.00345	7.50	0.00656	10.84	0.00370	23.43
0.00660	7.52	0.01123	10.75	0.00662	22.93
0.00932	7.52	0.01751	10.71	0.00993	22.47
0.01274	7.53	0.02464	10.67	0.01220	22.18
0.01728	7.54	0.03061	10.63	0.01557	21.80
0.02040	7.57	0.03763	10.58	0.02103	21.21
2 mol. % BD-1,2		*30 mol. % BD-1,2*		*90 mol. % BD-1,2*	
0.00246	6.32	0.00200	14.27	0.00347	24.14
0.00530	6.30	0.00937	13.93	0.00428	23.93
0.00722	6.28	0.01439	13.85	0.00653	23.51
0.00998	6.28	0.02007	13.72	0.00830	23.18
0.01325	6.26	0.02668	13.64	0.01271	22.42
0.01632	6.27	0.03140	13.56	0.01762	21.92
5 mol. % BD-1,2		*50 mol. % BD-1,2*		*95 mol. % BD-1,2*	
0.00298	5.73	0.00281	19.79	0.00191	25.10
0.00618	5.69	0.00638	19.41	0.00347	24.56
0.01222	5.61	0.00800	19.25	0.00413	24.39
0.02156	5.52	0.01149	18.91	0.00667	23.81
0.02901	5.48	0.01365	18.79	0.00897	23.39
0.03724	5.40	0.01756	18.58	0.01028	23.22
10 mol. % BD-1,2		*70 mol. % BD-1,2*		*100 mol. % BD-1,2*	
0.00599	6.99	0.00469	22.38	0.00250	24.94
0.01186	6.95	0.00883	21.80	0.00499	24.43
0.01875	6.94	0.01231	21.38	0.00781	23.72
0.02448	6.90	0.01716	20.84	0.01006	23.39
0.03046	6.89	0.01962	20.59	0.01245	23.05
0.03851	6.86	0.02198	20.38	0.01713	22.30

α is the degree of dissociation. Because

$$\Phi_{\mathrm{L}} = -\Delta H^{\ominus}_{\mathrm{dil}} = \Delta H_{\mathrm{m}} - \Delta H^{\ominus}_{\mathrm{m}} \qquad (2)$$

eqn. (1) can be rewritten as

$$\Delta H_{\mathrm{m}} - \alpha\Phi_{\mathrm{L}}(\mathrm{FI}) = \Delta H^{\ominus}_{\mathrm{m}} + (1-\alpha)\,\Delta H^{\ominus}_{\mathrm{A}} \qquad (3)$$

where ΔH_{m} is the experimentally determined molal enthalpy of electrolyte dissolution at given molality m and $\Delta H^{\ominus}_{\mathrm{m}}$ is the standard enthalpy of solution.

TABLE 3

Standard enthalpies of solution of NaI in water–BD-1,4 and water–BD-1,2 mixtures at 298.15 K, and the ionic-association constants in these systems

Mol.% diol	Water–BD-1,4			Water–BD-1,2		
	$-\Delta H^{\ominus}_{m}$ (kJ mol^{-1})	K_A (dm^3 mol^{-1})	$-\Delta H^{\ominus}_{m,corr}$ (kJ mol^{-1})	$-\Delta H^{\ominus}_{m}$ (kJ mol^{-1})	K_A (dm^3 mol^{-1})	$-\Delta H^{\ominus}_{m,corr}$ (kJ mol^{-1})
0	7.58			7.58		
2	6.96			6.43		
5	6.53			5.93		
10	6.46			7.31		
20	6.95			11.33		
30	10.12	2.4 [a]	10.10	14.66	4.6 [b]	14.64
50	15.76	4.6 [a]	15.76	20.55	12.3 [b]	20.68
70	20.82	7.0 [a]	20.84	23.90	28.8 [b]	24.39
80	23.24	9.0 [a,c]	23.27	24.96	34.0 [b,c]	25.43
90	25.50	10.8 [a]	25.58	25.87	48.5 [b]	26.41
95	26.37	11.5 [a,c]	26.47	26.43	51.0 [b,c]	26.77
100	27.15	12.3 [a]	27.46	26.57	55.8 [b]	27.03

[a] Values taken from ref. 6.

[b] Values taken from ref. 7.

[c] Interpolated value.

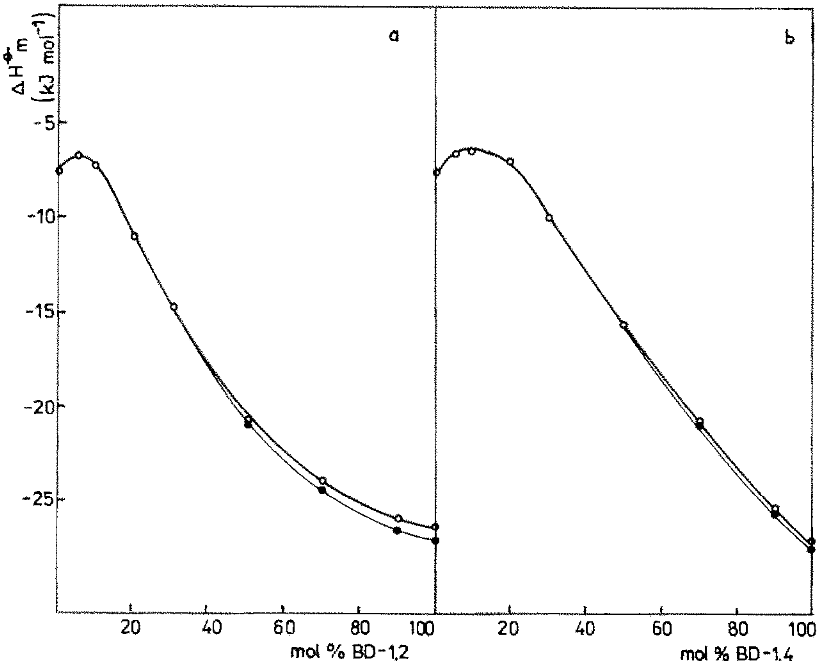

Fig. 1. "Corrected" (●) and "uncorrected" (○) standard solution enthalpies, $\Delta H^{\ominus}_{m}$ of NaI in (a) water–BD-1,2 and (b) water–BD-1,4 mixtures at 298.15 K.

The Φ_L(FI) values were calculated using the equation proposed by Barthel et al. [11]. The necessary values of the degree of the electrolyte dissociation were obtained from conductometric measurements. Therefore, the left-hand side of eqn. (3) can be calculated using the experimental data

$$\delta = \Delta H_m - \alpha\Phi_L(\text{FI}) \qquad (4)$$

Plotting δ as a function of $(1 - \alpha)$, we obtain for each examined mixture a straight line dependence

$$\delta = \Delta H_m^\ominus + (1 - \alpha)\,\Delta H_A^\ominus \qquad (5)$$

that extrapolated until $(1 - \alpha)$ equals zero gives the standard enthalpy of solution $\Delta H_m^\ominus$. The slope of the function is equal to the enthalpy of ionic association $\Delta H_A^\ominus$.

The redetermined standard enthalpies of NaI solution $\Delta H_{m,corr}^\ominus$ are given in Table 3. moreover, in Fig. 1 the corrected values of $\Delta H_m^\ominus$ are plotted as a function of the mixed solvent composition and compared with those extrapolated by using the previously mentioned Criss and Cobble method [8].

It follows from the data shown that the effect of ionic association in water–BD-1,4 solutions can be practically neglected. In contrast, in water–BD-1,2 systems starting from about 70 mol.% BD-1,2, the differences in both "corrected" and "uncorrected" values of the standard enthalpy of solution are visible, though no change in the curve shape is observed. One can assume that such changes in $\Delta H_m^\ominus$ are brought about by different structures of the investigated mixtures of water with BD-1,2 and water with BD-1,4. Our observations are confirmed by the results of Borghesani et al. [12], who have considered the coefficients of interactions of pairs in mixtures of water with all isomeric butandiols and concluded that in water–BD-1,2 systems the hydrophobic interactions play a considerable part.

In order to obtain a clearer idea about the phenomena occurring in the investigated systems it would be useful to supplement the studies by potentiometric measurements.

REFERENCES

1 S. Taniewska-Osińska, J. Woźnicka and L. Bartel, Thermochim. Acta, 47 (1981) 65.
2 J. Woźnicka and S. Taniewska-Osińska, J. Chem. Soc. Faraday Trans. 1, 79 (1983) 2879.
3 J. Woźnicka, S. Taniewska-Osińska and A. Bald, J. Chem. Soc. Faraday Trans. 1, 85 (1989) 3335.
4 G. DiPaola and B. Belleau, Can. J. Chem., 53 (1975) 3452.
5 G. Barone, B. Bove, G. Castranuovo and V. Elia, J. Solution Chem., 10 (1981) 803.
6 A. Bald, A. Szejgis, J. Woźnicka and M. Jóźwiak, J. Chem. Res., (S) (1992) 117; (M) (1992) 923.

7 A. Bald, A. Szejgis, J. Woźnicka and M. Jóźwiak, J. Chem. Res., (S) (1992) 249; (M) (1992) 2201.
8 C.M. Criss and J.W. Cobble, J. Am. Chem. Soc., 83 (1961) 3223.
9 H. Piekarski, Can. J. Chem., 61 (1983) 2203.
10 G.A. Krestov, I.V. Egorova and V.V. Korolev, Zh. Fiz. Khim., 59 (1985) 2327.
11 J. Barthel, H.J. Gores, G. Schneer and R. Wachter, Non-aqueous electrolyte solutions in chemistry and modern technology, Topics in Current Chemistry, Vol. 111, Springer-Verlag, Berlin, 1983.
12 G. Borghesani, R. Pedriali, F. Pulidori and I. Scaroni, J. Solution Chem., 15 (1986) 397.