Journal of Thermal Analysis, Vol. 54 (1998) 279-284

EXCESS ENTHALPIES OF BINARY MIXTURES OF FORMAMIDE WITH SECONDARY AMIDES

A. M. Zaichikov

Department of Inorganic Chemistry, Ivanovo State Academy of Chemical Technology
pr. Engelsa 7, 153460 Ivanovo, Russia

Abstract

The excess molar enthalpies H^E of binary mixtures of formamide with N-methylformamide, N-ethylformamide, N-methylacetamide, N-ethylacetamide and N-methylpropion-amide have been measured as functions of the mole fraction at 308.15 K, using an isoperibol rotating calorimeter. The experimental values of H^E are negative for all mixtures over the whole composition range. Intermolecular interactions in these mixtures are discussed through comparison of the results with those for corresponding binary mixtures of water.

Keywords: binary mixtures, excess enthalpies, formamide, secondary amides

Introduction

Intermolecular interactions in binary mixtures containing N-monosubstituted or secondary amides of aliphatic carboxylic acids are of considerable interest [1]. Excess enthalpies are very important for an understanding of the specificity of interactions in solutions because they directly reflect their energy. This work continues systematic studies of the thermodynamic properties of binary solutions of amides. It contains data on the enthalpies of mixing of formamide (FA) with N-methylformamide (NMF), N-ethylformamide (NEF), N-methyl-acetamide (NMA), N-ethylacetamide (NEA) and N-methylpropionamide (NMP) at 308.15 K. This temperature was chosen for measurements because NMA exists in the crystalline state at 298.15 K. Preceding communications were concerned with excess thermodynamic functions of aqueous solutions of primary, secondary and tertiary amides of carboxylic acids [2–6]. In [6, 7], the substitution of alkyl groups for amino group protons was shown to influence the enthalpies of mixing of amides with water substantially. Like water, FA molecules can form four hydrogen-bonds to produce three-dimensional associated structures in both the crystalline and liquid states [8, 9]. The effects of alkylation of primary amides on the enthalpies of their mixing with FA have not been studied thus far.

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

NMF (Aldrich), NEF (Fluka, Purum), NMA, NEA, NMP and FA of pure quality were purified by distillation under reduced pressure and then dried over a molecular sieve (Aldrich, 4A), except for FA, where molecular sieve 3A was used. After drying (NMA at 323 K), the liquid solvents were redistilled under vacuum. The water contents, determined according to Fisher's method, were less then 0.03 mass%. Excess molar enthalpies were measured with an isoperibol rotating calorimeter [10]. The experimental procedure and a test of the calorimetric system have been reported elsewhere [11]. The uncertainty in the determination of enthalpies is estimated to be less than 1%.

Results and discussion

The experimental values of H^E_{expt} for binary mixtures of FA with the N-alkylamides were approximated by Redlich-Kister polynomials:

$$H^E_{\text{calc}} = X_1 X_2 \sum_{n=1}^{p} C_n (X_1 - X_2)^{n-1} \tag{1}$$

where X_1 and X_2 are the mole fractions of the components. Here and below, the subscripts 1 and 2 designate FA or water and amides (NMF, NEF, NMA, NEA or NMP), respectively. The values of H^E_{expt} and coefficients C_i and the standard deviations of the approximations (1) are given in Table 1.

As Fig. 1 shows, the excess enthalpies are negative for the mixtures of FA with all these secondary amides. The values range between –560 and –210 J mol^{-1}. For comparison, the minima in the $H^E(X_2)$ curves of the water–N-alkylamide mixtures are at about –1820, –1330, –1000 and –940 J mol^{-1} at

Table 1 Excess molar enthalpies (J mol^{-1}) of formamide + N-alkyl-amide mixtures at 308.15 K

X_2	$-H^E$	X_2	$-H^E$	X_2	$-H^E$	X_2	$-H^E$
			FA – NMF				
0.0042	7.66	0.0188	32.86	0.2487	326.2	0.7939	262.4
0.0061	11.06	0.0307	52.21	0.3190	374.2	0.8497	202.1
0.0086	15.53	0.0511	85.53	0.4007	409.9	0.8958	146.4
0.0097	17.46	0.0706	115.3	0.4994	421.5	0.9308	100.4
0.0122	21.85	0.0951	151.4	0.5991	398.0	0.9479	76.93
0.0141	25.11	0.1646	241.4	0.7067	337.2	0.9748	38.40
0.0159	28.09						

C_1=–1684.08 C_2=–128.39 C_3=28.08 C_4=11.97 S=0.4

Table 1 Continued

X_2	$-H^E$	X_2	$-H^E$	X_2	$-H^E$	X_2	$-H^E$
FA – NMA							
0.0059	13.82	0.0202	45.11	0.1671	320.3	0.7104	435.1
0.0082	19.09	0.0252	55.38	0.2387	421.2	0.8019	329.7
0.0099	22.90	0.0303	67.07	0.3032	486.1	0.8998	180.8
0.0123	28.14	0.0479	105.9	0.3994	543.6	0.9201	148.2
0.0151	34.38	0.0705	148.8	0.4975	555.5	0.9470	101.9
0.0176	39.67	0.0984	203.7	0.6004	521.3	0.9702	59.31
$C_1=-2223.82$ $C_2=-241.95$ $C_3=92.09$ $C_4=110.76$ $S=1.0$							
FA – NMP							
0.0042	3.04	0.0279	18.67	0.2316	147.8	0.8039	125.7
0.0081	5.80	0.0314	21.21	0.3073	179.1	0.8840	80.25
0.0120	8.51	0.0516	36.09	0.3997	202.7	0.9167	58.98
0.0158	11.08	0.0744	52.50	0.5007	210.0	0.9469	39.35
0.0198	13.75	0.0998	71.26	0.6049	197.0	0.9731	20.72
0.0241	16.39	0.1501	103.2	0.7269	160.0		
$C_1=-838.05$ $C_2=-42.04$ $C_3=62.74$ $C_4=13.37$ $S=0.5$							
FA – NEF							
0.0099	12.50	0.1449	161.4	0.4954	327.9	0.8932	120.1
0.0299	36.37	0.2335	237.2	0.5995	312.9	0.9235	89.04
0.0521	62.49	0.3021	280.3	0.7015	268.2	0.9491	60.37
0.0771	90.98	0.3925	314.7	0.7990	205.0	0.9711	35.05
0.1027	119.5						
$C_1=-1311.67$ $C_2=-59.32$ $C_3=24.51$ $C_4=48.36$ $S=0.6$							
FA – NEA							
0.0113	12.75	0.1551	166.3	0.5015	337.1	0.8825	128.0
0.0319	35.97	0.2380	239.7	0.5988	320.1	0.9156	93.77
0.0539	60.93	0.3177	291.6	0.7104	265.7	0.9531	54.09
0.0749	84.83	0.4196	329.8	0.8003	202.3	0.9741	30.31
0.0998	111.1						
$C_1=-1349.41$ $C_2=-66.59$ $C_3=185.72$ $C_4=94.11$ $S=0.5$							

X_2 mole fraction of N-alkyl-amide;
C_i coefficients of Eq. (1), J mol^{-1};
S standard error, J mol^{-1}

308.15 K for NMA, NEA, NMF and NMP, respectively [6, 7]. The results can be qualitatively explained in terms of intermolecular interactions such as hydrogen-bonding. FA and secondary amides are known to be strongly associated liquids with intermolecular hydrogen-bonds. According to [12], the contribution of hydrogen-bonding in N-alkylamides amounts to about half of the total intermolecular energy, and in FA this is the predominant contribution.

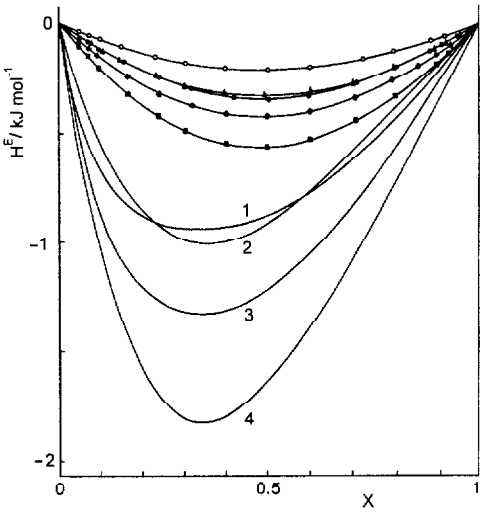

Fig. 1 Excess molar enthalpies of the mixtures: ○ – [(1–X)FA+XNMP]; s – [(1–X)FA+XNEF]; • – [(1–X)FA+XNEA]; ◆ – [(1–X)FA+XNMF]; ■ – [(1–X)FA+XNMA]; 1 – [(1–X)H_2O+XNMP] [7]; 2 – [(1–X)H_2O+XNMF] [6]; 3 – [(1–X)H_2O+XNEA] [7]; 4 – [(1–X)H_2O+XNMA] [6] at 308.15 K

The secondary amides largely consist of chains of various lengths formed by intermolecular hydrogen-bonds N–H···OC [8, 9, 13]. The carbonyl groups of FA and N-alkylamides are good proton acceptors and form heteroassociates C=O···H–N with each other. FA has two NH-protons, and one molecule of FA may form two hydrogen-bonds N–H···O with the molecules of the secondary amides. The negative excess enthalpies for the mixtures indicate that the endothermic contributions from the dissociation of FA and these N-alkylamides are more than compensated by the exothermic effects of interaction between the unlike molecules.

Enthalpies of solution of the components at infinite dilution in each other are presented in Table 2. They are calculated from the correlations

$$\Delta H_1^0 = \lim_{X_1 \to 0} \frac{\partial H^E}{\partial X_1} = \sum_{n=1}^{p} C_n(-1)^{n-1}, \qquad \Delta H_2^0 = \lim_{X_2 \to 0} \frac{\partial H^E}{\partial X_2} = \sum_{n=1}^{p} C_n \tag{2}$$

Table 2 Enthalpies of solution and enthalpic interaction coefficients in water and formamide at 308.15 K

Solute	Water			Formamide		
	ΔH_1^o/	ΔH_2^o/	h_{22}/	ΔH_1^o/	ΔH_2^o/	h_{22}/
	kJ mol^{-1}		J kg mol^{-2}	kJ mol^{-1}		J kg mol^{-2}
NMF	–1.6	–6.7	264±23	–1.5	–1.8	68±34
NEF	–	–		–1.2	–1.2	–
NMA	–3.7	–12.5	343±91	–2.0	–2.3	154±25
NEA	–2.9	–12.9		–1.2	–1.1	–
NMP	2.2	11.0	570±10[a)]	0.8	0.7	14±31

The coefficients of polynomials (1) are taken from Table 1 and previous studies [6, 7]. The negative values of H_1^o indicate that the hydrogen-bonds in water and FA that are broken on dissolution are replaced by stronger heterocomponent bonds. The absolute values of ΔH_1^o for water decrease in the sequence NMA> NEA>NMP>NMF, which agrees with those for the constants of association and the enthalpies of dimerization of secondary amides [14]. When data from [15, 16], are taken into account, this sequence indicates the relative strength of hydrogen-bonds between water or FA and N-alkylamides. The larger geometrical dimensions of the FA molecule in comparison with water hampers the formation of heterocomponent hydrogen-bonds with N-alkylamides. It leads to decreases in the absolute values of ΔH_1^o, ΔH_2^o and H^E (Fig. 1) in mixtures of FA with the secondary amides in comparison with those in aqueous solutions. The values of H^E for aqueous solutions of the secondary amides differ from each other significantly despite the small differences in the alkyl groups of the amides. We explained this fact by the considerable differences in the enthalpies of self-association and in the proton-accepting and proton-donating abilities of pure N-monosubstituted amides [6, 7]. The arrangement of the $H^E(X_2)$ curves in FA solutions correlates with the general tendency for an increase in the endothermic effect of mixing with increase in size or number of alkyl radicals. However, the worsening of the conditions for the heteroassociation leads to the approach of the enthalpies of mixing, which increase in the sequence NMA<NMF<NEA, NEF<NMP. The enthalpic pairwise interaction coefficients calculated from the H^E values by the method given in [17] are presented in Table 2. The coefficients h_{22} in FA are positive and smaller than those in water. Their magnitudes are considerably nearer to each other than those in water and must be the same for NEF and NEA. This possibly indicates the smaller structuring of FA around the hydrophobic groups of the secondary amides.

* * *

This research was supported in part by the Russian Foundation of Basic Research, grant N 96-03-33642.

References

1 Yu. M. Kessler and A. L. Zaitsev, Solvophobic Effects, Elis Horwood, Chichester 1994.
2 A. M. Zaichikov and G. A. Krestov, Russ. J. Phys. Chem., 69 (1995) 353.
3 A. M. Zaichikov and Yu. G. Bushuev, Russ. J. Phys. Chem., 69 (1995) 1766.
4 A. M. Zaichikov, Yu. G. Bushuev and G. A. Krestov, J. Thermal Anal., 45 (1995) 687.
5 A. M. Zaichikov and O. E. Golubinskii, Russ. J. Phys. Chem., 70 (1996) 1971.
6 A. M. Zaichikov and O. E. Golubinskii, Russ. J. Phys. Chem., 70 (1996) 1090.
7 A. M. Zaichikov, Russ. J. Gen. Chem., in press.
8 H. Ohtaki, S. Itoh and B. M. Rode, Bull. Chem. Soc. Jpn., 59 (1986) 271.
9 W. L. Jorgensen and C. J. Swenson, J. Am. Chem. Soc., 107 (1985) 569.
10 A. M. Zaichikov, O. E. Golubinskii and N. I. Zheleznyak, Izv. Vuzov. Khim. Khim. Technol., 33 (1990) 124.
11 A. M. Zaichikov, E. A. Nogovitsyn, N. I. Zheleznyak and G. A. Krestov, Russ. J. Phys. Chem., 62 (1988) 1630.
12 E. Z. Li, L. P. Zaichenko, A. A. Abramson, V. A. Proskuryakov and A. A. Slavin, Zh. Obshch. Khim., 54 (1984) 254.
13 K. Pralat, J. Jadzyn and S. Balanicka, J. Phys. Chem., 87 (1983) 1385.
14 M. Lindheimer, G. Etienne and D. Brun, J. Chim. Phys., 5 (1972) 829.
15 A. Burneau, J. Mol. Liq., 46 (1990) 99.
16 J. N. Spenser, S. K. Berger, C. R. Powell, B. D. Henning, G. G. Furman, W. M. Loffredo, E. M. Rydberg, R. A. Neubert, C. E. Shoop and D. N. Blanch, J. Phys. Chem., 85 (1981) 1236.
17 M. Bloemendal, K. Booij and G. Somsen, J. Chem. Soc. Faraday Trans., P. 1, 81 (1985) 1015.
18 A. Zielenkiewicz, Thermochim. Acta, 79 (1984) 371.