ELSEVIER

Thermochimica Acta 265 (1995) 55–62

thermochimica acta

Cryoscopic behavior in acetamide–zinc acetate dihydrate melts

R.M. Nikolić, M.D. Marinković

Chemistry Department, Institute of Nuclear Sciences "Vinča", P.O. Box 522, 11001, Belgrade, Serbia

Received 13 February 1995; accepted 5 May 1995

Abstract

The melting point depression in the mixtures of acetamide–zinc acetate dihydrate was measured by DSC in the concentration range 0–0.331 mole fraction of zinc acetate dihydrate. Two sets of measurements were obtained for the two crystalline forms with different melting points in which the melts crystallized. Eutectic mixtures also appeared in both crystalline forms. From the experimental melting point depression data and relevant thermodynamic parameters of pure acetamide, activity coefficients of both components were calculated. The results obtained for the two sets of measurements agreed within ± 5%. The Van't Hoff dissociation parameter was also calculated in the concentration range studied.

Keywords: Acetamide; Activity coefficients; DSC; Melting temperature depression; Zinc acetate dihydrate

1. Introduction

Molten acetamide is a very good solvent for many inorganic salts [1, 2]. The fact that a large number of acetamide – salt mixtures melt below 353 K with a high enthalpy of phase change makes them attractive for thermal energy storage [3, 4]. The cryoscopic behavior of acetamide as a solvent for organic compounds has also long been known [5]. The high concentration of various solutes in molten acetamide opens up possibilities for the studies of stepwise ligand association equilibria. In order to calculate the thermodynamic constants of these equilibria, it is necessary to know the thermodynamic activity of acetamide in the related solutions.

In this work, activities of acetamide were calculated from melting point depression data obtained by DSC measurements in the mixture acetamide–zinc acetate dihydrate

SSDI 0040-6031(95)02511-1

in the concentration range 0–0.331 mole fraction of zinc acetate dihydrate. The activities of zinc acetate dihydrate were also calculated by a simple method based on integration of an analytical relation between osmotic coefficients and concentration [6].

The calculations of activities from cryoscopic data are particularly convenient in acetamide–salt mixtures because it was shown that both acetamide and its mixtures with salts can solidify from the melts in two crystalline modifications: stable (trigonal) and metastable (orthorombic) [3, 4, 7, 8].

The two crystalline forms differ in melting point and in enthalpy of fusion. Hence, two sets of cryoscopic data which are required for activity calculations can be obtained and the two sets of the results can be compared.

2. Experimental

2.1. Materials

Reagent grade acetamide (Merck product) was recrystallized with ether from a saturated solution in ethanol and dried under vacuum at 333 K for at least five hours. Melting temperatures of 353.9 ± 1.2 K for the stable form and 343.1 ± 1.6 K for the metastable form of acetamide were obtained from DSC measurements [3]. Reagent grade zinc acetate dihydrate (Pliva-Zagreb product) was used without further purification, after its melting point of 510 ± 0.5 K was checked [9].

2.2. Procedure

Appropriate quantities of the components were melted together at 363 K in stoppered glass vessels containing 15–20 g of each acetamide–zinc acetate dihydrate mixture. Samples for DSC measurements contained 1–5 mg of each recrystallized mixture and were sealed in volatile aluminum sample pans in a dry box.

DSC measurements were carried out with a Perkin Elmer DSC 4 microcalorimeter equipped for subambient measurements. Measurements were made over 273–363 K at a heating rate of $5\,\mathrm{K\,min^{-1}}$. The temperature scale of the calorimeter was calibrated carefully with an indium standard sample to ± 0.2 K. The energy scale of the instrument was also calibrated with indium for various range settings to $\pm 0.4\,\mathrm{J \cdot g^{-1}}$. The maxima of the endothermic peaks were taken as the melting temperatures for samples of mass ≤ 2 mg [10]. For larger samples, however, extrapolations from DSC were made according to earlier reported recommendations [11, 12]. At least three samples were scanned in at least three thermal cycles.

3. Results and discussion

The melting point depression in both crystalline forms was calculated from the melting temperature of pure acetamide in the stable and metastable forms and from the melting temperatures of each acetamide – zinc acetate dihydrate mixture of defined composition. As found in earlier studies of other acetamide – salt mixtures [3, 4], in the mixtures studied in this work the stable crystalline form usually crystallized in samples prepared in quantities larger than 10 g. Samples containing a few milligrams, like those contained in the DSC sample pans, usually crystallized in the metastable modification and remained in the same modification for several months. Hence, the first melting diagram of each sample showed the melting point of the stable form, since it was obtained from the originally prepared batch of the mixture with a defined composition. The subsequent thermal cycles, reproduced in the DSC sample pans, showed melting peaks of the metastable modification with a lower melting point than the stable modification. Fig. 1. illustrates the difference in the melting diagrams, obtained by DSC, of the stable and metastable modifications of acetamide – zinc acetate dihydrate, containing 0.192 mol of the salt hydrate.

Formation of a eutectic mixture was observed in both crystalline forms. The dependence of the melting points of the acetamide–zinc acetate dihydrate mixtures in the concentration range studied is shown in Fig. 2 for both crystalline forms. The composition of the eutectic in the stable form was 0.715 CH_3COONH_2–0.285 $Zn(CH_3COO)_2 \cdot 2H_2O$, with a melting point of 312.6 ± 0.7 K, and 0.795 CH_3COONH_2–0.205 $Zn(CH_3COO)_2 \cdot 2H_2O$, with a melting point of 302.3 ± 0.7 K. The molten mixtures crystallized after significant supercooling. In the DSC samples, supercooling exceeded 10 K, while in larger, batch samples supercooling was less than 5 K. The melting points of the eutectics are in the desirable temperature range for solar energy storage applications. Other thermophysical properties which are significant for energy

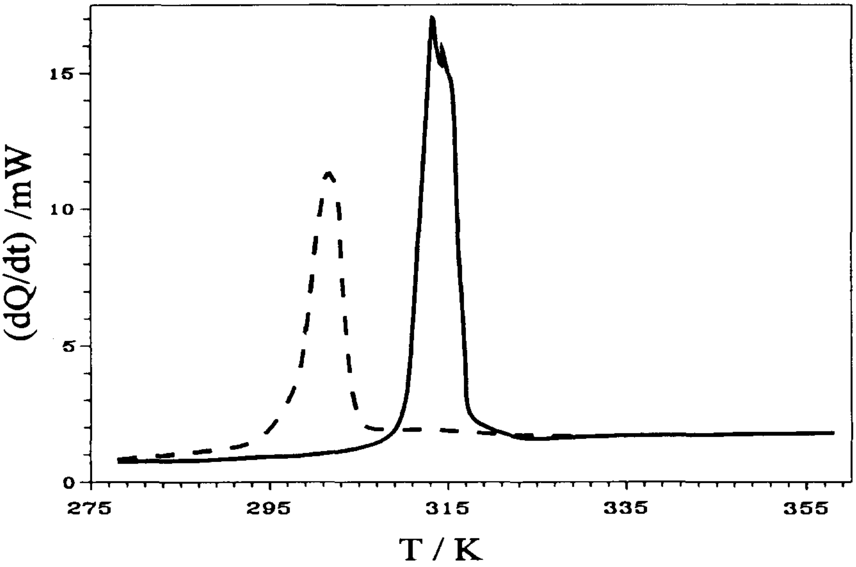

Fig. 1. DSC melting curves of the two crystalline forms of 0.808 CH_3COONH_2–0.192 $Zn(CH_3COO)_2 \cdot 2H_2O$.

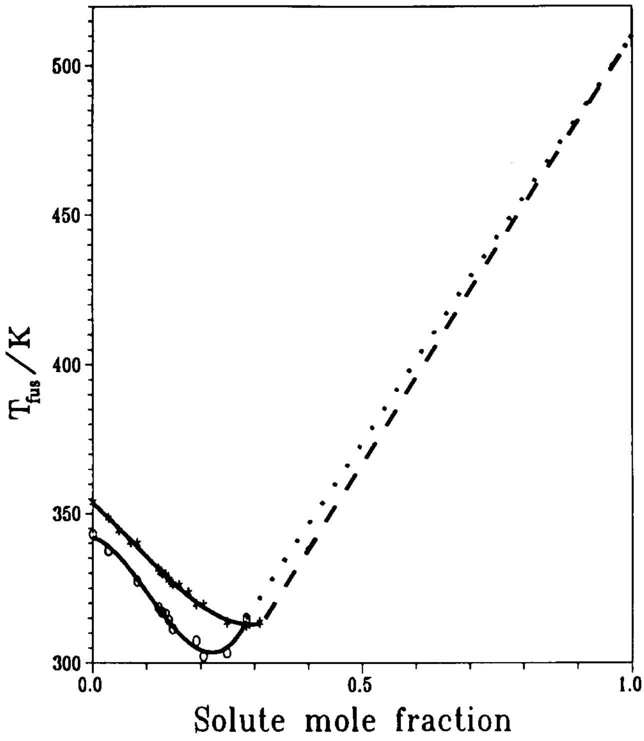

Fig. 2. The dependence of melting temperatures on the composition of CH_3COONH_2–$Zn(CH_3COO)_2$; ***-stable form; o o o-metastable form.

storage (enthalpy of melting and crystallization, heat storage density, thermal stability, seeding) will be presented in another paper.

The dependence of the melting points of the acetamide – zinc acetate dihydrate mixtures in the concentration range studied is shown in Fig. 2 for both crystalline forms. The mixtures containing more than 0.33 mole fractions of the salt component were very viscous, crystallized very slowly and were not convenient for DSC studies.

Cryoscopic constants K for the two crystalline forms of pure acetamide were calculated in an earlier work [13]. With experimental values of the melting point depression ΔT, obtained for each acetamide – zinc acetate dihydrate mixture and with known values of the cryoscopic constant K, the Van't Hoff dissociation factor i, showing the number of solute ions in the solvent, was calculated from relation

$$i = \frac{\Delta T}{K \cdot m} \qquad (1)$$

where m is the molality of the zinc acetate dihydrate solute. The following values for the cryoscopic constant were used for evaluation of i in this work [13]:

$K = 3.99\,\mathrm{K\,mol^{-1}}$ for the stable form, and
$K = 4.45\,\mathrm{K\,mol^{-1}}$ for the metastable form.

In Table 1 are presented the experimental values of ΔT and values of the factor i calculated from Eq. (1) for both crystalline forms. The results obtained for the two sets of measurements are in very good agreement. The values of the dissociation factor i gradually increased from nearly 3 in dilute solutions to nearly 4 when eutectic compositions were approached. This is an indication that in dilute solutions of the dihydrated zinc acetate in molten acetamide, water molecules are strongly coordinated to zinc ions, so that the hydrated salt acts as a pseudo-anhydrous salt with a large, hydrated cation. Similar behavior was observed in other studies of association equilibria with hydrated molten salts [14, 15]. With higher salt concentration, dissociation of the salt increases and the salt cations probably compete in association with the salt anions and the solvent molecules as indicated earlier from cryoscopic and ultrasonic measurements [16].

The calculation of the activity of acetamide from the DSC melting diagrams was made using the relation

$$\ln a_1 = -\left(\frac{\Delta H_{\mathrm{fus}} - \Delta C_p T_{\mathrm{fus}}}{R T_{\mathrm{fus}}}\right)\left(\frac{T_{\mathrm{fus}}}{T} - 1\right)\frac{\Delta C_p}{R}\ln\left(\frac{T_{\mathrm{fus}}}{T}\right) \tag{2}$$

where a_1 is the activity of acetamide, ΔH_{fus} and T_{fus} represent the enthalpy and the melting temperature of pure acetamide, T is the melting temperature of the mixture and Δc_p is the difference between the molar heat capacities of acetamide in the liquid and solid state. Measurements of the molar heat capacity of acetamide as a function of temperature in both crystalline forms and in the liquid state were made using a sapphire sample as standard [13, 17]. Hence, variation of the activity with composition follows

Table 1
Variation of melting point depression and dissociation factor with the molality of $Zn(CH_3COO)_2 \cdot 2H_2O$

m	ΔT/K (stable)	i (stable)	ΔT/K (metastable)	i (metastable)
0.4555	5.3	2.92	5.6	2.76
0.7243	9.5	3.29	–	–
0.9958	13.5	3.40	–	–
1.1390	13.9	3.06	15.7	3.09
1.5522	22.4	3.62	24.5	3.55
1.5964	23.4	3.67	25.8	3.63
1.6153	23.9	3.71	26.1	3.63
1.6739	24.4	3.65	26.6	3.57
1.7239	25.9	3.76	28.6	3.73
1.7936	27.4	3.83	31.6	3.96
1.8916	27.8	3.68	–	–
2.0265	30.4	3.76	–	–
2.1363	34.1	4.00	35.6	3.74
2.2304	34.5	3.88	40.8	4.11
2.5177	40.2	4.00	39.7	3.54
2.7201	41.3	3.80	28.1	2.32

from the variation of the melting point with composition. The method is very simple and it is claimed [6] that it enables calculation of activity values to a very high accuracy (0.2%) provided that accurate values of the relevant thermodynamic parameters are known. For acetamide – salt melt systems, as mentioned earlier, two sets of parameters required by Eq. (2) can be obtained from DSC measurements for the two crystalline forms in which the melts can crystallize.

The following values of the thermodynamic parameters of pure acetamide were used for calculation of the activity of acetamide [13]: for the stable form, $\Delta H_{\text{fus}} = 15535 \pm 600$ J/mol, $T_{\text{fus}} = 353.9 \pm 1.6$ K, $\Delta c_p = 53.76 \pm 0.70$ J/mol for the metastable form, $\Delta H_{\text{fus}} = 13113 \pm 500$ J/mol^{-1}, $T_{\text{fus}} = 343.1 \pm 1.6$ K, $\Delta c_p = 50.71 \pm 0.70$ J/mol.

The values of a_1 obtained from the two sets agreed within 5% in the low concentration range of the solute ($x_1 \leq 0.8$), before the eutectic composition was reached. In Table 2, the activity (a_1) and activity coefficients (γ_1) of acetamide in the mixtures with variable mole fraction (x_1) of acetamide are presented for both crystalline forms.

The activity of the solute can be calculated from known values of acetamide activities by an analytical method [6], using osmotic coefficients (ϕ_1) obtained from

$$\phi = \frac{\ln a_1}{r} \tag{3}$$

where a_1 is the activity of the solvent and r is the ratio of the mole fractions of solute (x_2) and solvent (x_1). The activity of zinc acetate dihydrate (a_2) was calculated from

$$\frac{\ln a_2}{r} = \phi_{(r)} - 1 + \int_0^r \frac{\phi - 1}{r} dr \tag{4}$$

Table 2
Activity and activity coefficients of CH_3COONH_2 in CH_3COONH_2–$Zn(CH_3COO)_2 \cdot 2H_2O$

x_1	a_1 (stable)	γ_1 (stable)	a_1 (metastable)	γ_1 (metastable)
0.971	0.9235	0.951	0.9273	0.955
0.953	0.8666	0.909	–	–
0.930	0.8151	0.876	–	–
0.918	0.8101	0.882	0.8076	0.880
0.878	0.7098	0.808	0.7144	0.813
0.873	0.6988	0.800	0.7014	0.803
0.871	0.6933	0.796	0.6985	0.802
0.865	0.6879	0.796	0.6935	0.802
0.859	0.6718	0.782	0.6742	0.785
0.851	0.6561	0.771	0.6460	0.759
0.840	0.6519	0.776	–	–
0.823	0.6254	0.760	–	–
0.808	0.5894	0.729	0.6100	0.755
0.795	0.5856	0.737	0.5658	0.712
0.751	0.5338	0.711	0.5750	0.765
0.715	0.5243	0.733	–	–

Table 3
Variation of osmotic coefficients of CH_3COONH_2 and activity of $Zn(CH_3COO)_2 \cdot 2H_2O$ with mole fraction of $Zn(CH_3COO)_2 \cdot 2H_2O$

x_2	ϕ (stable)	ϕ (metastable)	$\ln a_2$ (stable)	$\ln a_2$ (metastable)
0.0290	2.66	2.53	0.116	0.110
0.0484	2.82	–	0.249	–
0.0700	2.71	–	0.410	–
0.0823	2.35	2.38	0.482	0.465
0.1221	2.46	2.42	0.859	0.820
0.1226	2.47	2.44	0.907	0.867
0.1288	2.48	2.43	0.928	0.884
0.1352	2.39	2.34	0.980	0.933
0.1413	2.42	2.40	1.048	1.005
0.1487	2.41	2.50	1.126	1.082
0.1604	2.24	–	1.221	–
0.1774	2.18	–	1.399	–
0.1920	2.22	2.08	1.577	1.486
0.2052	2.07	2.20	1.700	1.671

The main problem in solving Eq. (4) is the integration of the relation $(\phi - 1)/r$ versus r which was attained in two steps. Firstly, by regression with a second-degree polynomial of the relation $r/(\phi - 1)$ versus r, the limiting value of the osmotic coefficient ϕ was obtained at zero concentration of the solute, for both crystalline modifications. The coefficients of the polynomial were $b(0) = 8.8406 \times 10^{-3}$, $b(1) = 3.1617 \times 10^{-1}$, $b(2) = 2.1652$, for the stable form; and $b(0) = 8.6532 \times 10^{-3}$, $b(1) = 3.9060 \times 10^{-1}$, $b(2) = 1.7465$ for the metastable form. The integration was then easily performed using a numericals program for integration based on the trapezoidal rule.

In Table 3, calculated values of $\ln a_2$ for mixtures with variable mole fractions of zinc acetate dihydrate (x_2) are presented for two sets of the results together with the corresponding osmotic coefficients of acetamide.

From Table 3 it is seen that the activity of zinc acetate dihydrate dramatically increases with concentration, indicating again strong interactions with solvent.

4. Conclusion

In this work it was shown that fairly accurate values of the activity coefficients of acetamide can be obtained from melting point depression data in the mixture of acetamide–zinc acetate dihydrate. The fact that both acetamide and its molten mixtures with the solute can crystallize in two crystalline forms is an advantage, because the calculations were made from two sets of measurements.

The activity of the solute was also calculated in the concentration range studied. The values obtained indicate the possibility of solute–solvent interactions.

The cryoscopic behavior of acetamide in this mixture is very pronounced and eutectic mixtures with melting temperatures of 312.6 ± 0.7 K for the stable form and 302.6 ± 0.7 K for the metastable form are formed. The eutectic mixtures can be of possible interest for solar energy storage as the latent heat of fusion.

References

[1] O.F. Stafford, J. Am. Chem. Soc., 55 (1933) 3987.

[2] G. Jander and G. Winkler, J. Inorg. Nucl. Chem., 9 (1959) 24.

[3] R. Nikolić, J. Tripković and D.H. Kerridge, Thermochim. Acta, 146 (1989) 353.

[4] R. Nikolić, G. Ristić and M. Todorović, Solar Energy Materials and Solar Cells, 28 (1992) 59.

[5] E. Cherbuliez and G. de Mandrot, Helv. Chim. Acta, 14 (1931) 183.

[6] G.N. Lewis and M. Randall, in K.S. Pitzer and L. Brewer (Eds.), Thermodynamics, McGraw Hill, New York, 2nd edn., 1961, Chap. 20.

[7] F. Senti and D. Harker, J. Am. Chem. Soc., 62 (1940) 2008.

[8] W.C. Hamilton, Acta Crystallogr., 18 (1965) 866.

[9] R.C. Weast (Ed.), Handbook of Chemistry and Physics, CRC, Cleveland, 49th edn., 1968.

[10] E. Pella and M. Nebuloni, J. Therm. Anal., 3 (1971) 229.

[11] P. Franzosini and M. Sanesi, Thermal Methods, in D.G. Lovering and R.J. Gale (Eds.), Molten Salt Techniques, Vol. 1, Plenum, New York, 1983.

[12] G.W.H. Hohne, H.K. Cammenga, W. Eysel, E. Gmelin and W. Hemminger, Thermochim. Acta, 160 (1990) 1–12.

[13] R. Nikolić and G. Ristić, J. Solution Chem., 23 (1994) 787.

[14] C.A. Angell, J. Electrochem. Soc., 112 (1965) 1224.

[15] J. Braunstein, J. Phys. Chem., 71 (1967) 3402.

[16] G. Berchiesi, G. Gioia Lobbia, M.A. Berchiesi and G. Vitali, J. Thermal Anal., 29 (1984) 729.

[17] M.J. O'Neill, Anal. Chem., 38 (1966) 1331.