ELSEVIER

Thermochimica Acta 276 (1996) 17–25

thermochimica
acta

Cryoscopic behavior in the binary mixtures of acetamide–sodium acetate and acetamide–sodium acetate trihydrate

R. Nikolić *, M. Marinković, M. Pavlović

Chemistry Department, The Institute of Nuclear Sciences, Vinča, P.O. Box 522, 11001 Belgrade, Yugoslavia

Received 26 July 1995; accepted 20 October 1995

Abstract

The melting point depression of acetamide on addition of anhydrous sodium acetate and sodium acetate trihydrate was followed by DSC. Two sets of measurements were made for two crystalline forms in which the melts crystallized. From cryoscopic data, activity coefficients of acetamide were calculated in the concentration range 0 to 0.390 mole fraction of sodium acetate and 0 to 0.376 mole fraction of sodium acetate trihydrate. Activities of the salt components were calculated from the activities of the solvent using a simple analytical method. From melting point depression data and the known molar cryoscopic constant of acetamide, the Van't Hoff dissociation factor was calculated for both anhydrous and hydrated sodium acetate in the concentration ranges studied.

Keywords: Acetamide; Activity coefficients; DSC; Melting point depression; Sodium acetate

1. Introduction

The cryoscopic behavior of acetamide as a solvent for organic and inorganic compounds has long been known [1–3]. Owing to its pronounced cryoscopic behavior with water [4], it was proposed as a de-icing agent [5]. It was shown that a large number of acetamide salt mixtures with melting points below 80°C can be prepared [3, 6]. Recently, systematic studies of the melting point depression of acetamide in mixtures with some inorganic salts showed that fairly accurate values of the ther-

---

* Corresponding author. Fax: 38-11/444-0195.

Elsevier Science B.V.
SSDI 0040-6031(95)02774-2

modynamic activity of acetamide and some of the solutes can be calculated from cryoscopic studies [7, 8]. A possibility that acetamide and its binary mixtures can crystallize in two different crystalline forms with different melting points and other different thermodynamic properties was shown to be an advantage in using this method for calculation of the activities from two independent sets of measurements.

In this work, melting point depression of acetamide with addition of two inorganic salts was followed by DSC: anhydrous sodium acetate in the concentration range 0 to 0.390 mole fraction and sodium acetate trihydrate in the concentration range 0 to 0.376 mole fraction of the salt component. In addition, a mixture containing 0.103 mole fraction of acetamide in sodium acetate trihydrate, proposed for heat storage [9], was also studied. The dependence of the activities of acetamide on the solute concentration in both mixtures was calculated from cryoscopic data. Activities of the solutes in both mixtures were also calculated.

2. Experimental

2.1. Materials

Reagent grade acetamide (Merck product) was recrystallized and dried as described earlier [7, 8]. Its purity was checked from melting point measurements by DSC for stable (trigonal) and metastable (orthorhombic) crystalline forms (353.9 ± 1.2 K and 343.1 ± 1.6 K, respectively). Reagent grade sodium acetate trihydrate (Merck product) was used without further purification, while anhydrous sodium acetate was obtained by careful dehydration of the hydrated salt in a vacuum dryer with gradual increase of temperature from 323 to 423 K, and finally dried on a vacuum line at 423 K for five hours. The purity of both salts was checked by melting point measurements. The values obtained from DSC measurements agreed with the tabulated data to within ± 0.5 K (331 K for sodium acetate trihydrate and 597 K for anhydrous sodium acetate) [10].

2.2. Procedure

The mixtures of the desired composition were prepared by melting together at 363 K appropriate quantities of components in stoppered glass vessels containing about 20 g of acetamide–salt mixture. Samples for DSC measurements were prepared in a dry box from each recrystallized mixture. These samples contained 1–5 mg and were sealed in aluminum pans for volatile samples. At least three samples of each mixture were scanned in at least three thermal cycles over the temperature range 273–363 K.

DSC measurements were carried out with a Perkin-Elmer DSC 4 calorimeter with a sub-ambient accessory. The temperature scale was calibrated with an indium standard sample to ± 0.2 K, while the energy scale was calibrated for various energy settings to ± 0.4 J. g^{-1}, also using indium standard samples.

The maxima of the endothermic peaks for samples with mass ≤ 2 mg were taken as the melting temperatures [11]. For larger samples, extrapolations from DSC endothermic peaks were made according to the recommendations reported elsewhere [12, 13].

The agreement in the melting point temperature determinations for various samples of the same mixture was within ±0.3 K.

3. Results and discussion

The dependence of the melting temperatures on the composition of the mixtures acetamide–sodium acetate and acetamide–sodium acetate trihydrate, in the studied concentration ranges, is shown in Figs. 1 and 2, respectively.

From Fig. 1, it can be seen that eutectic mixtures are formed in both crystalline forms: at 0.2258 mole fraction of sodium acetate in the stable form with a melting temperature of 318.9 ± 1.1 K, and at 0.2157 mole fraction of sodium acetate in the metastable form with a melting temperature of 310.1 ± 0.9 K. The mixtures exhibit a significant supercooling effect (more than 10 K in the samples of ≤ 1 g). The mixtures with compositions containing higher concentrations of sodium acetate are very viscous and they are not suitable for studies by DSC.

From Fig. 2, it can be concluded that eutectic formation also occurs in the mixtures of acetamide with sodium acetate trihydrate in both crystalline forms. Furthermore, the mixtures containing higher concentrations of the solute component crystallized in the stable form only. These mixtures showed significant supercooling without seeding agents, but the melting temperature of the eutectics and high values of the enthalpy of

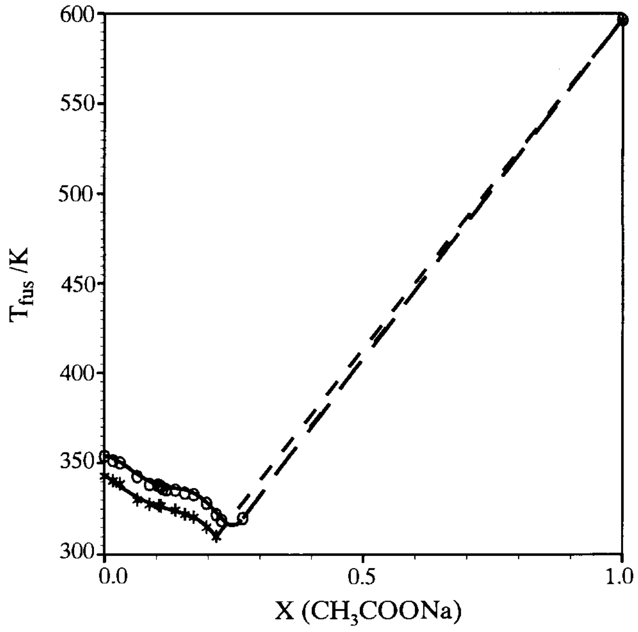

Fig. 1. The dependence of melting temperatures on the composition of acetamide–sodium acetate (anhydrous); ○○○ - stable form; *** - metastable form.

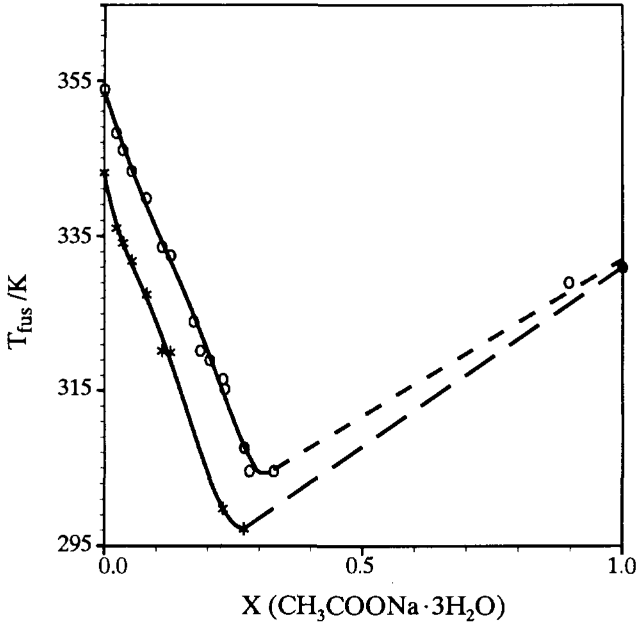

Fig. 2. The dependence of melting temperatures on the composition of acetamide–sodium acetate trihydrate; ○○○ - stable form, *** - metastable form.

fusion make these mixtures very promising as latent heat or solar energy storage media. The study of the properties relevant to energy storage for various acetamide–salt acetate mixtures will be the subject of another paper.

Similarly to earlier studies [8], melting point depression (ΔT) was calculated for both acetamide–salt mixtures studied and in both crystalline forms. The conditions for appearance of the two forms in pure acetamide and in acetamide–salt mixtures were described elsewhere [6, 7]. The following values of melting points of pure acetamide were taken in the calculations [14]: stable form, 353.9 ± 1.2 K; metastable form, 343.1 ± 1.6 K.

The melting temperatures of each mixture of the defined composition were subtracted from the melting points of pure acetamide in the corresponding crystalline form. From the calculated ΔT values and the literature values of the cryoscopic constant K of acetamide in the two crystalline forms [7], the Van't Hoff dissociation factor i expressing the number of solute ions in the solvent was calculated from the relation

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

where m is the molality of the solute.

The following values of the cryoscopic constant K were taken in the calculations of i: stable form, $K = 3.99$ K mol^{-1}; metastable form, $K = 4.45$ K mol^{-1}.

In Tables 1 and 2, variations of the melting point depression ΔT and dissociation factor i with the molality of the solutes m are presented for the mixtures of acetamide–sodium acetate and acetamide–sodium acetate trihydrate, respectively.

Table 1
Variation of melting point depression and dissociation factor with molality of sodium acetate (anhydrous)

m	ΔT/K (stable)	i (stable)	ΔT/K (metastable)	i (metastable)
0.2755	2.4	2.18	2.5	2.04
0.4852	3.6	1.86	4.2	1.94
1.0411	11.0	2.65	12.9	2.78
1.4653	15.3	2.62	15.5	2.38
1.6981	15.7	2.32	–	–
1.7152	15.8	2.31	16.0	2.10
1.7603	16.4	2.33	16.1	2.06
1.7835	16.5	2.32	16.4	2.07
1.8286	17.7	2.42	–	–
1.9176	18.2	2.38	–	–
2.1980	18.3	2.09	18.7	1.91
2.4698	19.9	2.02	21.0	1.91
2.7308	20.8	1.91	22.4	1.84
3.0964	25.6	2.07	28.0	2.03
3.3695	31.9	2.37	33.0	2.20
3.5146	35.0	2.50	–	–
4.0936	33.9	2.08	–	–

Table 2
Variation of melting point depression and disssociation factor with molality of sodium acetate trihydrate

m	ΔT/K (stable)	i (stable)	ΔT/K (metastable)	i (metastable)
0.3865	5.7	3.67	5.0	2.91
0.5813	7.9	3.26	8.4	3.25
0.8392	10.6	3.16	11.3	2.54
1.2463	14.1	2.83	15.6	2.81
1.6483	20.3	3.09	22.9	3.12
1.8570	21.4	2.89	23.1	2.79
2.3846	29.9	3.14	31.1	2.93
2.5272	33.7	3.34	–	–
2.7263	34.9	3.21	–	–
2.9938	37.2	3.11	43.3	3.25
3.0262	38.7	3.20	–	–
3.3620	42.3	3.15	45.9	3.07
3.3862	42.4	3.14	–	–
3.8859	49.3	3.18	–	–

The results obtained for the two sets of measurements in both systems are in very good agreement. The values of the dissociation factor i are ≈ 2 for the system acetamide–sodium acetate and ≈ 3 for the system acetamide–sodium acetate trihydrate. In contrast to the behavior observed in the systems acetamide–calcium nitrate [7] and acetamide–zinc acetate dihydrate [8], the values of i are not changed significantly in the concentration range studied. The values of i indicate that only the salt components are dissociated into sodium cations and acetate anions and that the hydrated water acts as a polarized ion.

The calculation of the activity of acetamide from melting point depression data was made using the relation

$$\ln a_1 = -\left(\frac{\Delta_{\text{fus}}H - \Delta C_p T_{\text{fus}}}{R T_{\text{fus}}}\right)\cdot\left(\frac{T_{\text{fus}}}{T} - 1\right)\cdot\frac{\Delta C_p}{R}\ln\left(\frac{T_{\text{fus}}}{T}\right) \tag{2}$$

where a_1 is the activity of acetamide, $\Delta_{\text{fus}}H$ and T_{fus} are the enthalpy of fusion and the melting temperature of pure acetamide, and T is the melting temperature of the mixture. The difference between the molar heat capacity of acetamide in the liquid and solid state, ΔC_p, was taken from earlier measurements of heat capacity variation with temperature for both crystalline forms of pure acetamide, using a sapphire sample as a standard [7, 15]. From two sets of parameters, required by Eq. (2), two sets of activity data were obtained for each mixture in both systems studied.

The following values of the thermodynamic parameters of pure acetamide were used for the calculation of the activity of acetamide [7, 14]: stable form, $\Delta_{\text{fus}}H = 15535 \pm 600$ J mol^{-1}, $T_{\text{fus}} = 353.9 \pm 1.2$ K, $\Delta C_p = 53.76 \pm 0.70$ J mol^{-1} K^{-1}; metastable form, $\Delta_{\text{fus}}H = 13113 \pm 500$ J mol^{-1}, $T_{\text{fus}} = 343.1 \pm 1.6$ K, $\Delta C_p = 50.71 \pm 0.70$ J mol^{-1} K^{-1}.

Variation of the activity and the activity coefficients of acetamide in the mixtures of acetamide–sodium acetate (anhydrous) and acetamide–sodium acetate trihydrate with mole fraction of acetamide, x_1, are given in Tables 3 and 4, respectively, for both crystalline forms.

The values of the activity of acetamide (a_1) and the activity coefficients (γ_1) for the two sets of calculations in each mixture agreed within $\pm 3\%$ in the low concentration

Table 3
Activity and activity coefficients of acetamide in acetamide–sodium acetate (anhydrous)

x_1	a_1 (stable)	γ_1 (stable)	a_1 (metastable)	γ_1 (metastable)
0.984	0.9640	0.979	0.9670	0.983
0.970	0.9475	0.977	0.9451	0.974
0.937	0.8469	0.904	0.8394	0.896
0.910	0.7928	0.871	0.8099	0.890
0.896	0.7879	0.879	–	–
0.895	0.7855	0.878	0.8043	0.899
0.892	0.7795	0.874	0.8032	0.900
0.890	0.7782	0.874	0.7998	0.900
0.887	0.7639	0.861	–	–
0.881	0.7580	0.860	–	–
0.863	0.7568	0.877	0.7747	0.898
0.845	0.7382	0.873	0.7515	0.889
0.828	0.7279	0.879	0.7357	0.888
0.803	0.6750	0.841	0.6799	0.846
0.784	0.6106	0.779	0.6333	0.807
0.774	0.5809	0.751	–	–
0.733	0.5913	0.807	–	–

Table 4
Activity and activity coefficients of acetamide in acetamide–sodium acetate trihydrate

x_1	a_1 (stable)	γ_1 (stable)	a_1 (metastable)	γ_1 (metastable)
0.976	0.9180	0.941	0.9087	0.931
0.964	0.8879	0.921	0.8854	0.918
0.947	0.8521	0.900	0.8580	0.906
0.919	0.8076	0.879	0.8087	0.880
0.889	0.7336	0.825	0.7306	0.822
0.872	0.7211	0.827	0.7286	0.835
0.827	0.6305	0.762	–	–
0.815	0.5932	0.728	–	–
0.796	0.5818	0.731	–	–
0.770	0.5606	0.728	0.5456	0.709
0.767	0.5471	0.713	–	–
0.729	0.4828	0.662	0.5252	0.720
0.720	0.4593	0.638	–	–
0.672	0.4593	0.683	–	–
0.624	0.5040	0.808	–	–

range of the solutes. It is observed that the deviation from ideality is more pronounced in the mixture containing the hydrated salt.

The activities of the solutes were calculated from the activity values of acetamide and the osmotic coefficient (ϕ), obtained from the relation

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

where r is the ratio of mole fractions of solute (x_2) and solvent (x_1). The osmotic coefficient (ϕ) is related to the activity of solute through the equation

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

The solution of Eq. (4) was made in two steps. In the first step, regression with a second-order polynomial of the relation $r/(\phi - 1)$ versus r, the limiting value of the osmotic coefficient ϕ at zero concentration of the solute, was obtained for both crystalline forms. In the second step, the integration was performed using a numerical program for integration based on the trapezoidal rule. The following coefficients of the polynomial for the mixture acetamide–sodium acetate (anhydrous) were obtained: $b(0) = 1.7589 \times 10^{-2}$, $b(1) = 3.0022 \times 10^{-1}$, $b(2) = 4.5633$, for the stable form; and $b(0) = 2.8749 \times 10^{-2}$, $b(1) = -5.1324 \times 10^{-1}$, $b(2) = 11.8310$, for the metastable form. For the mixture acetamide–sodium acetate trihydrate, the coefficients of the polynomial were: $b(0) = 1.2897 \times 10^{-2}$, $b(1) = 1.7487 \times 10^{-1}$, $b(2) = 2.7787$ for the stable form; and $b(0) = 1.0529 \times 10^{-2}$, $b(1) = 2.6759 \times 10^{-1}$, $b(2) = 2.6069$ for the metastable form.

Variations in the osmotic coefficient and the activity of the solutes in the mixtures acetamide–sodium acetate (anhydrous) and acetamide–sodium acetate trihydrate are presented in Tables 5 and 6, respectively. The agreement of the results for activity data in two independent sets of measurements in both the systems studied was within ± 6%.

Table 5
Variation of osmotic coefficients of acetamide and activity of sodium acetate with mole fraction of sodium acetate

x_2	ϕ (stable)	ϕ (metastable)	ln a_2 (stable)	ln a_2 (metastable)
0.0164	2.24	2.01	0.0345	
0.0300	1.74	1.82	0.0649	0.0278
0.0630	2.48	2.61	0.2467	0.0650
0.0896	2.36	2.15	0.3711	0.2689
0.1044	2.04	–	0.4498	0.3962
0.1055	2.04	1.85	0.4545	–
0.1084	2.04	1.88	0.4733	0.4605
0.1089	2.03	1.81	0.4812	0.4815
0.1128	2.12	–	0.5108	0.4816
0.1194	2.04	–	0.5432	–
0.1367	1.76	1.61	0.6118	–
0.1547	1.66	1.57	0.7113	0.6162
0.1721	1.53	1.48	0.8016	0.7210
0.1969	1.60	–	0.9925	0.8128
0.2157	1.79	–	1.1860	–
0.2258	1.86	–	1.2881	–
0.2669	1.44	–	1.4995	–
				–

Table 6
Variation of osmotic coefficients of acetamide and activity of sodium acetate trihydrate with mole fraction of sodium acetate trihydrate

x_2	ϕ (stable)	ϕ (metastable)	ln a_2 (stable)	ln a_2 (metastable)
0.0235	3.55	2.80	0.1186	0.0852
0.0360	3.19	3.04	0.1970	0.1642
0.0530	2.86	2.73	0.2667	0.2663
0.0814	2.41	2.40	0.4551	0.4595
0.1115	2.47	2.52	0.7261	0.7339
0.1280	2.23	2.16	0.8497	0.8385
0.1726	2.21	–	1.3029	–
0.1854	2.29	–	1.4635	–
0.2038	2.12	–	1.6362	–
0.2298	1.94	1.79	1.8998	1.8391
0.2331	1.98	–	1.9523	–
0.2680	1.81	1.77	2.3496	2.3137
0.2706	1.80	–	2.4408	–

4. Conclusion

In the present work, it is shown that both sodium acetate and sodium acetate trihydrate cause significant melting point depression of acetamide. In both systems eutectic mixtures are formed and the compositions of the eutectics were defined for both crystalline forms in which the melts crystallized. From the melting point depression values, three parameters were calculated: (a) The Van't Hoff dissociation factor i which was ≈ 2 for acetamide–sodium acetate and ≈ 3 for acetamide–sodium acetate trihydrate and did not change significantly in the concentration range studied (Tables 1 and 2). The effect is opposite to the results obtained for acetamide mixtures with salts containing metal ions with high charge density (Ca^{2+}, Zn^{2+}) [7, 8]. (b) The activity of acetamide in both mixtures showed gradual decrease with increasing concentration of the solutes until the eutectic compositions were reached. The change in the solvent activity was more pronounced in the melt with the hydrated salt as solute (Tables 3 and 4). (c) The activity of the solutes was calculated from the known values of the solvent activity in the both mixtures studied. The activity of the solutes gradually increased with increasing concentration of the solutes. The effect is more pronounced in the melt with sodium acetate trihydrate (Tables 5 and 6).

References

[1] E. Cherbuliez and G. de Mandrot, Helv. Chim. Acta, 14 (1931) 183.
[2] F. Castellani, G. Berchiesi, F. Pucclarelli and V. Bartocci, J. Chem. Eng. Data, 26 (1981) 150.
[3] G. Berchiesi, G. Gioia Lobbia, V. Bartocci and G. Vitali, Thermochim. Acta, 70 (1983) 317.
[4] P.M. Bugai and V.P. Slinko, Zh. Fiz. Khim., 45 (1971) 996.
[5] R. Vogel, German Patent DE 3434953, 1986.
[6] R. Nikolić, G. Ristić and M. Todorović, Solar Energy Materials and Solar Cells, 28 (1992) 59.
[7] R. Nikolić and G. Ristić, J. Solution Chem., 23 (1994) 787.
[8] R. Nikolić and M. Marinković, Thermochim. Acta, 265 (1995) 55.
[9] K.K.K. Eslen and S. Kiya, Jpn. Kokai Tokhyo JP 60 06 781, 1985.
[10] R.C. Weast, M.J. Astle and W.H. Beyer, (Eds.), Handbook of Chemistry and Physics, 69th edn., CRC Press Inc., Boca Raton, 1988–1989.
[11] E. Pella and M. Nebuloni, J. Therm. Anal., 3 (1971) 229.
[12] G.W.H. Hohne, H.K. Cammenga, W. Eysel, E. Gmelin and W. Hemminger, Thermochim. Acta, 160 (1990) 1.
[13] P. Franzosini and M. Sanesi, Thermal Methods, in: D.G. Lovering and R.J. Gale (Eds.), Molten Salt Techniques, Vol. 1, Plenum Press, New York, 1983.
[14] R. Nikolić, J. Tripković and D.H. Kerridge, Thermochim. Acta, 146 (1989) 353.
[15] M.J. O'Neill, Anal. Chem., 38 (1966) 1331.