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Heat capacities of sodium carbonate–sodium bicarbonate aqueous solution mixtures

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Abstract

Enthalpies of mixing of isomolal Na_2CO_3 and $NaHCO_3$ aqueous solutions were measured in the 0.1–1.0 molality and 293–328 K temperature range using a flow-mix microcalorimetric cell. Heat capacities of the mixture were calculated from a slope of the dependence of the enthalpy of mixing on temperature, and the values obtained varied in the range from -0.019 to -0.105 $J\,kg^{-1}\,K^{-1}$. The heat capacity versus molality curve shows a minimum corresponding to the electrolyte molality for which complete ion hydration is attained.

Keywords: Enthalpy; Heat capacity; Sodium bicarbonate; Sodium carbonate

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1. Introduction

It is well known [1–3] that flow calorimetric measurements are mostly performed in order to obtain the enthalpies of dilution and heat capacities of single electrolyte solutions at 30 MPa and temperatures up to 600 K.

Our previous work [4] on the enthalpy of mixing of sodium carbonate and sodium bicarbonate aqueous solutions has shown that our flow-mix microcalorimetric cell is suitable for direct heat of mixing measurements at temperatures not exceeding 353 K. The enthalpies obtained by mixing solutions with a common small, structure-making Na^+ ion are shown to be endothermic (positive). Further, it is assumed that the Na^+–HCO_3^- pair and Na^+–Na^+–CO_3^{2-} triplet are the most probable structures formed during the mixing process, which may be the reason for the marked asymmetry obtained. It is also noted that the enthalpy of mixing has a maximum at 308 K and then

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decreases as the temperature rises; an assumption that the primary hydration sphere around the Na^+ ion breaks down with increasing temperature explains the phenomenon.

In trying to clarify structural changes in the aqueous medium during the mixing of Na^+, bicarbonate and carbonate ions (important constituents of natural water systems), we thought it would be of interest to determine the heat capacities of the Na_2CO_3–$NaHCO_3$ mixture. We therefore continued our work by measuring the enthalpies of mixing of isomolal Na_2CO_3 and $NaHCO_3$ aqueous solutions using the same flow-mix microcalorimetric cell. From the enthalpy of mixing temperature dependence we determined the heat capacities of mixtures and then considered the form of the curve of heat capacity versus molality.

2. Experimental

Mixing experiments were performed in the flow-mix cell of the Thermometric (LKB) multichannel microcalorimeter described previously [5]. Calibration was performed by means of an electrical heater in the flow cell.

Reagent grade $NaHCO_3$ (Merck) was thermally pretreated at 383 K for 24 h; the reagent grade $Na_2CO_3 \cdot 10H_2O$ was used without previous treatment. All the solutions used were isomolal and were prepared with freshly boiled, doubly distilled water. The molal fraction of the components in the mixture was 0.5, and the solutions to be mixed were not of the same molal ionic strength.

The molality of the solutions was checked by titration with a standard 0.1 *m* HCl solution.

The solutions were introduced into the, flow-mix cell by a pair of microperpex peristaltic pumps previously calibrated with the same solutions. The flow rate of each pump was 15 ml h^{-1}, so attaining a molar fraction of both salts of 0.5.

The solution densities were measured with an AP Paar calculating density meter, model DMA 55.

Measurements were performed in the 293–328 K temperature range, but were not continued at higher temperatures because of the appearance of air bubbles.

3. Results and discussion

The enthalpy of mixing values, each calculated as a mean value from three experimental runs, together with the uncertainty intervals obtained as twice the standard deviation of the mean value are presented in Table 1. The experimental error for lower temperatures (up to 308 K) did not exceed 6%, but for some higher temperatures (318 and 328 K) it reached 16%.

It is obvious from Table 1 that, for all the molalities studied, the enthalpy of mixing decreases with increasing temperature, even becoming negative (exothermic) for higher temperatures. What is surprising here is that the enthalpy of mixing values for 1.0 *m* solutions are lower than for 0.8 and 0.5 *m*. In spite of this, the enthalpy of mixing temperature dependence is linear for mixtures of 1.0, 0.8 and 0.5 *m* solutions, enabling

Table 1
Enthalpies of mixing of isomolal Na_2CO_3 and $NaHCO_3$ aqueous solutions at different temperatures

Molality m in (mol per kg H_2O)	Temperature T in K	ΔH_m in (J per kg H_2O)	ΔH_m in (J per mol Na_2Co_3 $10H_2O$)
0.1	293	0.42 ± 0.03	8.44 ± 0.52
	298	0.43 ± 0.02	8.36 ± 1.66
	308	0.16 ± 0.01	3.19 ± 0.10
0.3	293	2.80 ± 0.08	19.15 ± 0.52
	298	0.90 ± 0.03	6.15 ± 0.18
	308	$-(0.59 \pm 0.01)$	$-(1.19 \pm 0.13)$
	318	$-(1.19 \pm 0.13)$	$-(8.12 \pm 0.90)$
0.5	293	5.74 ± 0.32	23.98 ± 1.34
	298	4.45 ± 0.12	18.61 ± 0.45
	303	3.74 ± 0.39	15.62 ± 1.63
	308	2.63 ± 0.16	11.00 ± 0.66
0.8	298	5.08 ± 0.15	13.59 ± 0.40
	308	3.40 ± 0.32	9.12 ± 0.86
	318	2.07 ± 0.06	5.57 ± 0.14
	328	0.54 ± 0.09	1.45 ± 0.24
1.0	298	2.05 ± 0.08	4.48 ± 0.18
	308	1.07 ± 0.08	2.34 ± 0.18
	328	$-(1.09 \pm 0.08)$	$-(2.37 \pm 0.16)$

the heat capacities to be calculated from the slope. For mixtures consisting of 0.3 and 0.1 m electrolytes the enthalpy of mixing temperature dependence has the form

$$\Delta H_m = a + bT + cT^2$$

which can be differentiated with respect to temperature, thus obtaining the dependence of the heat capacity of the mixture on temperature. However, as the 0.3 and 0.1 m solutions are quite dilute and the enthalpies of mixing were determined with an appreciable error, approximate heat capacity values for these mixtures were (despite the bad linear regression coefficients) calculated from the slope of "linear dependence" $\Delta H_m = f(T)$.

The heat capacities calculated for each pair of isomolal solutions studied, together with the linear regression coefficients, are given in Table 2.

The heat capacity of the Na_2CO_3–$NaHCO_3$ mixture is related to the electrolyte molality m in Fig. 1.

It is obvious from Fig. 1 that the heat capacity exhibits a minimum for 0.5 m solutions, a dependence already known from the literature [6, 7]. The ions in diluted solutions are surrounded by a primary hydration sphere, meaning the water molecules strongly associated with the ion, and then by a region of structure-broken water lying between the ion hydration sphere and the bulk water with its original structure. On mixing dilute solutions, it is assumed that there is an interchange of water molecules between the ions, causing the heat of mixing effect. The higher the concentration of the mixing solutions, the more the water molecules, first from the bulk water and then from

Table 2
Heat capacities of mixtures composed of isomolal Na_2CO_3 and $NaHCO_3$ aqueous solutions for different salt molalities

Molality m in (mol per kg H_2O)	$-\Delta C_p$ in ($J\,kg^{-1}\,K^{-1}$)	Regression coefficient r
0.1	0.019	−0.912
0.3	0.151	−0.941
0.5	0.201	−0.994
0.8	0.149	−0.999
1.0	0.105	−0.999

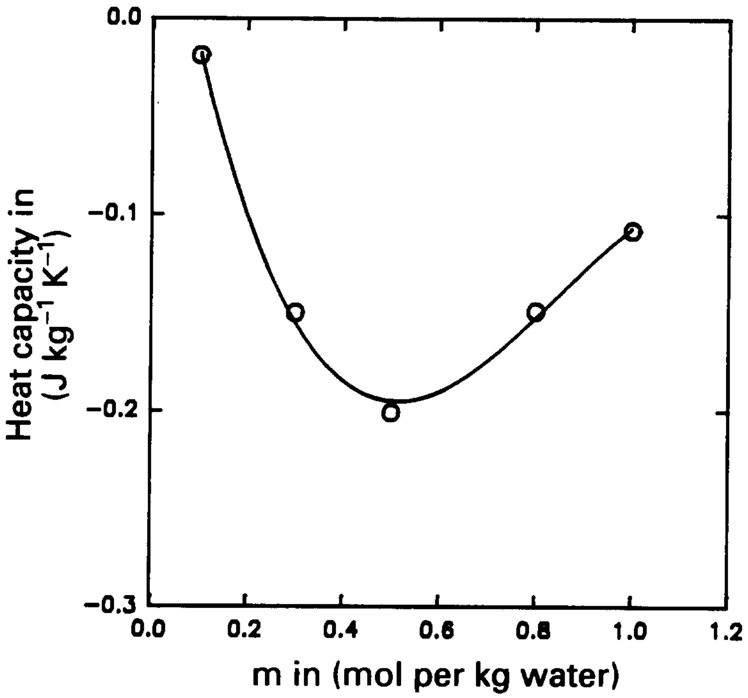

Fig. 1. Heat capacity of the Na_2CO_3–$NaHCO_3$ mixture as a function of electrolyte molality m.

the structure-broken region, are attracted by the ions, until the concentration is reached at which ion hydration is complete. The heat capacity decreases with increasing concentration, in confirmation of the redistribution of water molecules, which happens when two isomolal electrolyte solutions are mixed [7]. Further increase of molality also increases the heat capacity, which may be a consequence of ion dehydration and, probably, a more pronounced formation of ion complexes. We assumed earlier that the Na^+–HCO_3^- ion pair and Na^+–Na^+–CO_3^{2-} triplet were the most likely ion complexes formed during mixing at higher concentrations. As the upper solution concentration limit was determined by the saturation of the less soluble component, we were unfortunately unable to broaden the concentration range studied.

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