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Heat capacity measurements on sodium alkoxides

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Abstract

Heat capacity measurements of sodium alkoxides, namely sodium methoxide, sodium ethoxide, sodium *n*-propoxide and sodium iso-propoxide were carried out using differential scanning calorimetry (DSC) in the temperature range 240–550 K. From the heat capacity values, other thermodynamic functions, such as enthalpy increments, entropies and Gibbs energy functions of these compounds were derived and reported for the first time. The $C_{\mathrm{p,m}\,298}$ of sodium methoxide, sodium ethoxide, sodium *n*-propoxide and sodium iso-propoxide were measured and found to be 65.05, 90.87, 113.52 and 121.20 $\mathrm{J\,K^{-1}\,mol^{-1}}$ respectively.

Keywords: Sodium methoxide; Sodium ethoxide; Sodium *n*-propoxide; Sodium iso-propoxide; Heat capacity

1. Introduction

Liquid sodium is used as coolant and stainless steels are used as structural materials in fast breeder reactors [1,2]. During the operation of the reactor, a thin adherent layer of sodium is formed over the inner surface of the steel components in the coolant circuit due to wetting. During reactor maintenance, some of the stainless steel components are taken out for maintenance or replacement. Exposure of sodium wetted components to air could lead to fire and possible explosion as the reaction between sodium and moisture present in air is highly exothermic in nature. In addition to being a fire hazard, the reaction also acts adversely on the mechanical properties of the steel components due to the formation of sodium hydroxide resulting in caustic stress corrosion. To mitigate these problems, the sodium wetted small components are generally cleaned using lighter alcohols, such as methanol, ethanol, propanol, etc. [3–6] and also with heavier alcohols, such as butyl cellosolve (butoxy ethanol) [7–9] and ethyl carbitol (di ethylene glycol mono ethyl ether or 2,2-ethoxy ethoxy ethanol) [10,11]. Sodium alkoxide is the reaction product of sodium–alcohol reaction. For better understanding of the reactions and for avoiding any possible run-away reaction that might be caused due to the formation of sodium alkoxides [10,11], thermochemical properties, such as enthalpies of reaction, formation, dissolution and heat capacity are needed to be determined. Since there are no data on heat capacity of sodium alkoxides, heat capacity measurements were carried out on sodium methoxide, sodium ethoxide, sodium *n*-propoxide and sodium iso-propoxide, using differential scanning calorimetry (DSC) in the temperature range 240–550 K.

2. Experimental

2.1. Chemicals

Nuclear grade sodium (purity: 99.5%) from M/s Alkali Metals Pvt. Ltd., India, was further purified by vacuum distillation [12]. HPLC grade methanol (purity: 99.8%), iso-propanol (purity: 99.7%) from M/s Ranbaxy Fine Chemicals Ltd., India, absolute ethanol (purity: 99.9%) from M/s Hayman, UK and AR grade *n*-propanol (purity: >99.5%) from M/s S.D. Fine Chem. Ltd., India, were further purified by distillation [13] and used for the preparation of sodium methoxide, sodium ethoxide, sodium *n*-propoxide and sodium iso-propoxide. The reaction of sodium metal with alcohol to yield the respective sodium alkoxide was performed under argon atmosphere using a vacuum tight glass vessel. The details of preparation and characterization of these sodium alkoxides are described elsewhere [14]. However, a brief description is given below.

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2.2. Preparation of compound

$$\mathrm{Na} + \mathrm{ROH}_{\mathrm{excess}} \rightarrow [\mathrm{RONa}]_{\mathrm{ROH}} + \tfrac{1}{2}\mathrm{H}_2 \quad (\mathrm{R} = \text{methyl, ethyl, } n\text{- and iso-propyl}) \qquad (1)$$

$$[\mathrm{RONa}]_{\mathrm{ROH}} \xrightarrow{\text{Vacuum distillation}} \mathrm{RONa} \qquad (2)$$

About 150 mL of alcohol was taken in a reaction vessel and solid sodium pieces ranging from 300 to 500 mg were added. When alcohol reached near saturation, addition of sodium was stopped. Excess alcohol was removed by vacuum distillation at room temperature for about 6 h and then the temperature of the reaction vessel was gradually increased to 350 K for complete removal of alcohol. Free flowing milky white powder of sodium alkoxide was obtained and stored in argon atmosphere glove box. The formation of sodium alkoxides and their purity were confirmed by various analytical techniques, namely IR spectroscopy, powder X-ray diffraction and atomic emission spectroscopy, which are described elsewhere [14].

2.3. Equipment

A heat flux type differential scanning calorimeter, model DSC 821e/700 of M/s Mettler Toledo GmbH, Switzerland, was used in this study for heat capacity measurements.

2.4. Calorimetric measurements

The temperature calibration was carried out by measuring the melting temperature of indium, tin, lead and zinc at different heating rates 2, 5, 10 and 20 K min^{-1}. The onset temperature of melting at different heating rates were plotted against the heating rates and extrapolated to zero heating rate. The values of the extrapolated onset temperature at zero heating rate is used for temperature calibration. The heat flow calibration

Table 1
Heat capacity and thermodynamic functions of the sodium alkoxides

Compound T (K)	$C_{\mathrm{p,m}}$ (J K^{-1} mol^{-1})		$H^\circ_{\mathrm{T}} - H^\circ_{298}$ (J mol^{-1})	S°_{T} (J K^{-1} mol^{-1})	$-(G^\circ_{\mathrm{T}} - H^\circ_{298})/T$ (J K^{-1} mol^{-1})
	Measured	Fit			
Sodium methoxide					
250	59.26	59.27	−2995	99.64	111.62
298.15	65.05	65.05	0	110.58	110.58
300	65.37	65.27	121	110.98	110.58
350	71.20	70.87	3525	121.47	111.39
400	76.37	76.26	7204	131.28	113.27
450	81.66	81.52	11149	140.57	115.79
500	87.57	86.72	15355	149.43	118.72
550	91.56	91.86	19820	157.93	121.90
Sodium ethoxide					
250	82.33	82.00	−4168	124.48	141.15
298.15	90.90	90.87	0	139.70	139.70
300	90.96	91.19	168	140.26	139.70
350	99.50	99.16	4931	154.93	140.84
400	107.46	106.48	10074	168.65	143.47
450	112.82	113.43	15573	181.60	146.99
500	119.67	120.14	21413	193.90	151.07
550	126.90	126.70	27585	205.66	155.51
Sodium *n*-propoxide					
250	102.17	101.75	−5187	146.96	167.71
298.15	113.52	113.52	0	165.90	165.90
300	113.57	113.95	210	166.61	165.90
350	125.35	125.23	6193	185.03	167.33
400	136.15	136.01	12725	202.46	170.64
450	147.68	146.50	19789	219.08	175.11
500	156.64	156.82	27372	235.06	180.31
550	169.36	167.02	35469	250.48	185.99
Sodium iso-propoxide					
250	109.29	109.31	−5550	134.72	156.92
298.15	121.20	121.20	0	155.00	155.00
300	121.72	121.65	225	155.75	155.00
350	134.73	133.94	6615	175.42	156.52
400	146.57	146.20	13618	194.11	160.06
450	157.76	158.45	21235	212.04	164.85
500	170.73	170.68	29463	229.36	170.44
550	182.51	182.91	38303	246.20	176.56

was done by using enthalpy of melting of indium, tin, lead and zinc. The calibration experiments were performed at a heating rate of 10 K min^{-1}. National Institute of Standards and Technology (NIST) standard materials have been used for the above mentioned calibration. The heat flow rate calibration was performed using a disc of sapphire supplied by M/s Mettler Toledo GmbH, Switzerland. Heat flow rate calibration was done prior to every single run of the sample.

The samples for DSC measurements were pelletized using a hand toggle press and hermetically sealed in 40 μL aluminium pans. As the alkoxides are extremely sensitive towards moisture, sealing was done in an argon atmosphere glove box. Ultra high pure (99.999%) argon gas was used as the purge gas in the DSC measurements. DSC measurements on all the samples were carried out in the temperature range 240–550 K using a heating rate of 10 K min^{-1} and a purge gas flow rate of 50 mL min^{-1}. A disc of sapphire was used as the heat capacity standard. A three-segment heating program was used in these measurements. The first segment lasting for 5 min was an isothermal one at initial temperature; the second segment was a dynamic one with a heating rate of 10 K min^{-1} and the final segment lasting for 5 min was another isothermal one at the final temperature. The weight of the pan with sample was measured before and after completion of the heat capacity measurements and it was observed that there was no change in weight, which indicated that the sealing of the pan was leak tight.

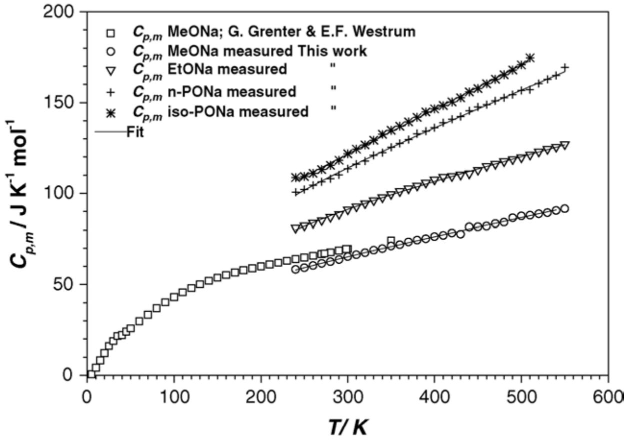

Fig. 1. Plot of heat capacity as a function of temperature of sodium alkoxides.

3. Results and discussions

The heat capacity data of sapphire given by National Institute of Standards and Technology, USA, was used for calibration. The heat capacity data of sodium methoxide, sodium ethoxide, sodium *n*-propoxide and sodium iso-propoxide measured by DSC in the present work and given in Table 1 are the mean values of five or six measurements. The relative standard deviations of the measured data for all the four compounds are in the range of 1–3%. The measured heat capacity values of sodium methoxide, sodium ethoxide, sodium *n*-propoxide and sodium iso-propoxide were fitted to a polynomial by least-squares method and are given in Table 2. The goodness of the fit was determined by computing the standard error using the following expression:

$$\text{Standard error}^2 = \frac{\left(\Sigma(C_{\text{p,m}}\,\text{measured} - C_{\text{p,m}}\,\text{fit})\right)^2}{\text{no. of observations} - \text{no. of coefficients}} \quad (3)$$

The standard error for sodium methoxide, ethoxide, *n*-propoxide and iso-propoxide are 0.52, 0.59, 0.76 and 0.83 J K^{-1} mol^{-1}, respectively.

The measured data along with the fit values for all the above sodium alkoxides are shown in Fig. 1. The heat capacity data of sodium methoxide measured by Grenter and Westrum [15]

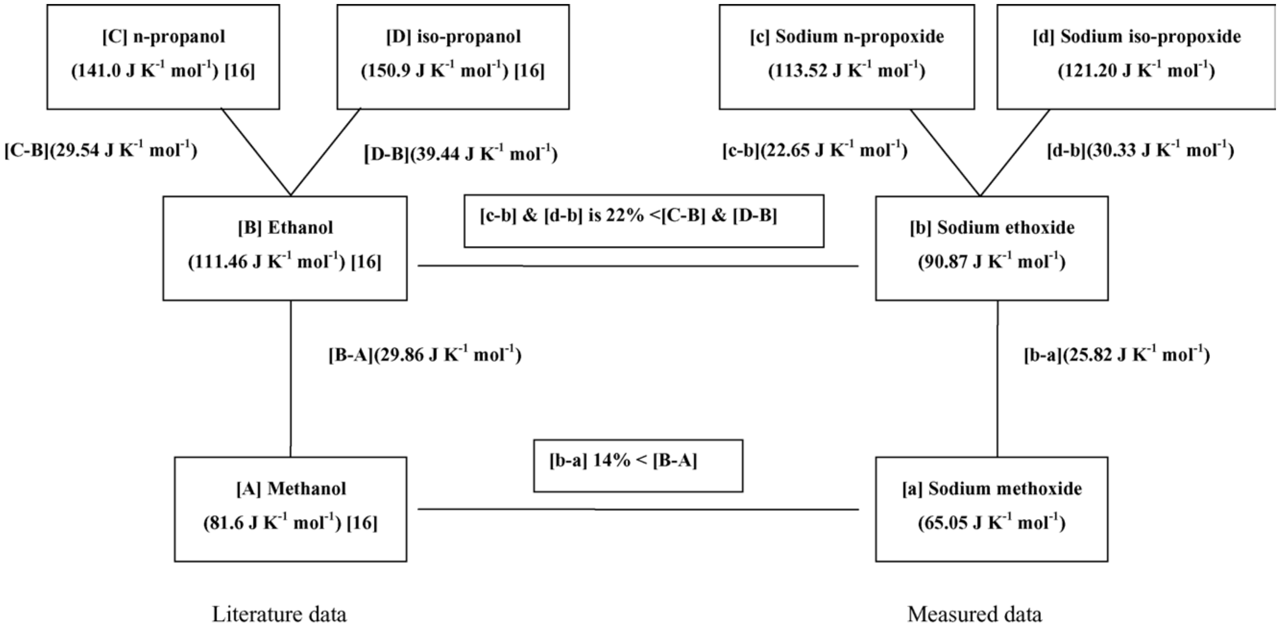

Fig. 2. Comparison of $C_{\text{p,m 298}}$ values of alcohols and sodium alkoxides.

Table 2
Heat capacity of sodium alkoxides fitted in the form of polynomial in temperature range 240–550 K

Compound	$C_{p,m}$ (240–550 K) ($J\,K^{-1}\,mol^{-1}$)	Standard error ($J\,K^{-1}\,mol^{-1}$)
Sodium methoxide	$37.52 + 1.0002 \times 10^{-1}\,T - 2.03107 \times 10^{5}\,T^{-2}$	0.52
Sodium ethoxide	$61.42 + 1.2247 \times 10^{-1}\,T - 6.27439 \times 10^{5}\,T^{-2}$	0.59
Sodium *n*-propoxide	$60.04 + 1.9738 \times 10^{-1}\,T - 4.76971 \times 10^{5}\,T^{-2}$	0.76
Sodium iso-propoxide	$48.69 + 2.442 \times 10^{-1}\,T - 2.6535 \times 10^{4}\,T^{-2}$	0.83

using low temperature adiabatic calorimeter are also shown in Fig. 1. As can be seen in the figure, the heat capacity of sodium methoxide measured in the present study is 4–6% less than that of Grenter and Westrum [15] in the overlapping temperature region.

From the fitted equations for heat capacity for sodium methoxide, ethoxide, *n*-propoxide and iso-propoxide, the enthalpy increments, entropies and Gibbs energy functions were computed and are given in Table 1 along with the measured $C_{p,m}$ values. S°_{298} values of the sodium alkoxides are needed for computing the entropy values from heat capacity data. But, S°_{298} value of sodium methoxide alone is available in literature, and hence those of other alkoxides were estimated as described below.

From the literature data on $C_{p,m\,298}$ [16] of alcohols, the $\Delta C_{p,m\,298}$ for the addition of one $-CH_2-$ group was computed. Similarly, the $\Delta C_{p,m\,298}$ for the addition of one $-CH_2-$ group was computed from the present data for the corresponding alkoxides and is shown in Fig. 2. It is assumed that the ratio of corresponding ΔS°_{298} values will also be same. As can be seen in Fig. 2, the contribution to increase in heat capacity towards the addition of one $-CH_2-$ group to sodium methoxide is 14% less than that of the alcohol counterpart. Similarly, the contribution to increase in heat capacity towards the addition of one $-CH_2-$ group to sodium ethoxide in the form of straight chain (forming sodium *n*-propoxide) and branched chain (forming sodium iso-propoxide) is 22% less than that of corresponding alcohols.

The S°_{298} values of methanol, ethanol, *n*-propanol and iso-propanol as well as that of sodium methoxide are available in the literature [16]. Using these values and the variation in $\Delta C_{p,m\,298}$ values shown in Fig. 2, the S°_{298}values of sodium ethoxide,

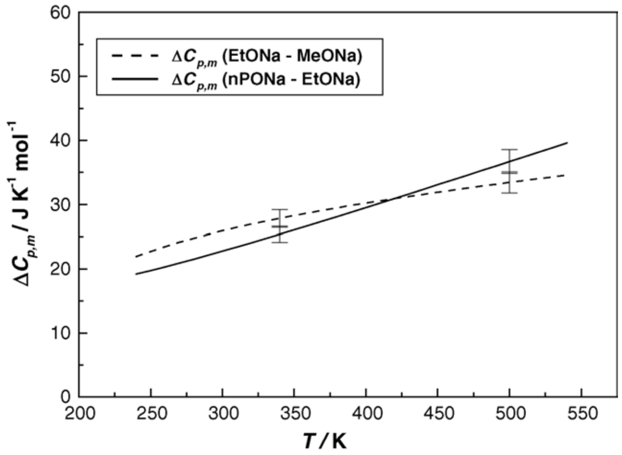

Fig. 4. Contribution to the increase in heat capacity due to the addition of one $-CH_2-$ group to sodium methoxide and sodium ethoxide.

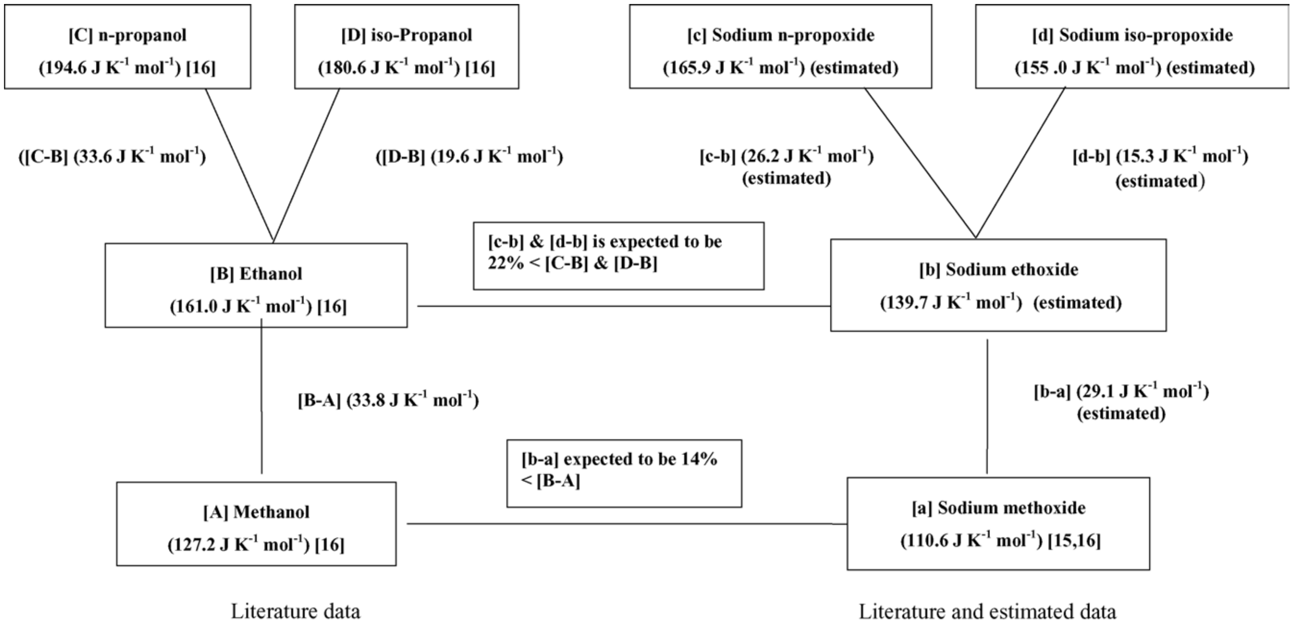

Fig. 3. Estimation of S°_{298} values of sodium alkoxides from that of alcohols.

n-propoxide and iso-propoxide were estimated as shown in Fig. 3.

Fig. 4 shows the variation in $\Delta C_{p,m}$ as a function of temperature for addition of one $-CH_2-$ to sodium methoxide as well as to sodium ethoxide. It can be inferred that $\Delta C_{p,m}$ for addition of one $-CH_2-$ group can be considered to be same for both the alkoxides. Therefore, from this study the heat capacity values of higher alkoxides such as sodium *n*-butoxide and sodium *n*-pentoxide can be estimated.

4. Conclusions

Heat capacity measurements were carried out on sodium alkoxides using DSC in the temperature range 240–550 K. Heat capacity of sodium methoxide from room temperature to 550 K was measured for the first time. The present data are the first one for the heat capacity of sodium ethoxide, sodium *n*-propoxide and sodium iso-propoxide. From these measurements, heat capacity values of higher sodium alkoxides can be estimated.

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