Note

APPARENT MOLAR HEAT CAPACITIES AND VOLUMES OF AQUEOUS SODIUM PROPIONATE

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(Received 26 June 1984)

As part of a continuing program of measurements leading to thermal and volumetric properties of aqueous electrolytes, we have used a flow calorimeter and a flow densimeter for measurements on aqueous sodium propionate over a wide range of concentrations. Results of these measurements have been used for calculations of apparent molar heat capacities and apparent molar volumes.

EXPERIMENTAL

All the heat capacity measurements were made with a Picker flow calorimeter [1] which was checked as previously recommended [2]. Densities of solutions were measured with a Picker flow densimeter [3]. The results of all of these measurements apply to 298.15 K.

Samples of sodium propionate were prepared from reagent-grade material by recrystallization, washing with ethanol, and drying in a vacuum desiccator. Solutions for measurement were prepared from known masses of sodium propionate and distilled water, with some further solutions being prepared by dilution of the primary solutions with distilled water.

RESULTS

The results of measurements with the Picker flow calorimeter are heat capacities per unit volume of solution. These heat capacities have been combined with the measured densities and the previously known heat capacity of water for calculation of the apparent molar heat capacity of

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dissolved sodium propionate, which is represented by $C_{p,\phi}$. Similarly, the densities of solutions in combination with the previously known density of water have yielded apparent molar volumes that are represented by V_ϕ. For both these calculations, equations of the following type were used

$$Y_\phi = \left[Y(\text{soln.}) - n_1 Y_1^0 \right] / n_2 \tag{1}$$

in which $Y(\text{soln.})$ is the extensive property (heat capacity or volume) of a specified quantity of solution, n_1 is the amount (moles) of water in this specified quantity of solution, Y_1^0 is the molar property (heat capacity or volume) of pure water, and n_2 is the amount (moles) of sodium propionate in the specified quantity of solution.

Our experimental results have been used as outlined above to obtain the apparent molar heat capacities and volumes of aqueous sodium propionate listed in Table 1. The measured heat capacities can be recovered from these tabulated $C_{p,\phi}$ values and corresponding molalities of solutions by way of

$$c_p = \left(m C_{p,\phi} + c_p^0 \right) / (1 + m M_2) \tag{2}$$

Similarly, densities of solutions can be recovered from the tabulated V_ϕ values and corresponding molalities by way of

$$\rho = (1 + m M_2) \rho_1^0 / \left(1 + m \rho_1^0 V_\phi \right) \tag{3}$$

In these equations c_p and c_p^0 are the specific heat capacities of solution and pure water, respectively, m is the molality of the solution, M_2 is the molar mass of sodium propionate, and ρ_1^0 is the density of pure water. For the calculations, the values of $c_p^0 = 4.1793$ J K^{-1} g^{-1} and $\rho_1^0 = 0.997044$ g cm^{-3} were used.

Apparent molar properties of dilute solutions of strong electrolytes are

TABLE 1

Apparent molar heat capacities and volumes of aqueous sodium propionate at 298.15 K

m (mol kg^{-1})	$C_{p,\phi}$ (J K^{-1} mol^{-1})	V_ϕ (cm^3 mol^{-1})
0.019474	150	53.68
0.039496	150	53.67
0.042083	154.8	53.82
0.10099	156.5	54.22
0.29562	166.3	54.72
0.59952	177.6	55.17
0.61358	180.1	55.18
0.89680	186.6	55.52
1.4144	200.5	56.00
1.6301	205.9	56.18

represented accurately by equations of the form

$$Y_\phi = Y_\phi^0 + A_Y \left(\rho_1^0 m\right)^{1/2} + B_Y m \qquad (4)$$

in which Y_ϕ^0 is the value of Y_ϕ at infinite dilution, A_Y is the limiting slope derived from the Debye–Hückel theory, m is the molality, and B_Y is an adjustable parameter. For our calculations with equations of type (4), we have used

$$A_C \left(\rho_1^0\right)^{1/2} = 28.95 \text{ J K}^{-1} \text{ mol}^{-3/2} \text{ kg}^{1/2} \text{ and } A_V \left(\rho_1^0\right)^{1/2}$$

$$= 1.865 \text{ cm}^3 \text{ mol}^{-3/2} \text{ kg}^{1/2}$$

It is also noted that partial molar properties of solutes, Y_2, can be obtained from corresponding apparent molar properties by way of

$$Y_2 = Y_\phi + m \left(\mathrm{d} Y_\phi / \mathrm{d} m\right) \qquad (5)$$

This equation shows that $Y_2^0 = Y_\phi^0$ at infinite dilution where $m = 0$.

Least-squares fits of equations of type (4) using the $C_{p,\phi}$ and V_ϕ values listed in Table 1 have led to the following results for aqueous sodium propionate at 298.15 K: $C_{p,2}^0 = C_{p,\phi}^0 = 145.6$ J K^{-1} mol^{-1}; $B_C = 17$ J K^{-1} mol^{-2} kg; $V_2^0 = V_\phi^0 = 53.4$ cm^3 mol^{-1}; and $B_V = 0.9$ cm^3 mol^{-2} kg.

On the basis of previous experience with the Picker calorimeter and densimeter and present considerations of purity of sodium propionate, it is estimated that uncertainties in the present $C_{p,2}^0$ and V_2^0 values are ± 5 J K^{-1} mol^{-1} and ± 0.6 cm^3 mol^{-1}, respectively.

Ackermann and Schreiner [4] measured heat capacities of relatively concentrated (0.5 − 2.24 m) solutions of sodium propionate at 20 and 30°C. Parker's analysis [5] of these results led her to select $C_{p,2}^0 = 158$ J K^{-1} mol^{-1} at 25°C. Primarily because of the absence of heat capacities for solutions more dilute than 0.5 m, the uncertainty in this value is larger than the difference (12 J K^{-1} mol^{-1}) between this value and the present $C_{p,2}^0 = 145.6$ J K^{-1} mol^{-1}.

More recently, Cabani et al. [6] reported $C_{p,2}^0 = 177.0$ J K^{-1} mol^{-1} for aqueous ammonium propionate at 25°C, based on heat capacities of solutions ranging from 0.4 to 2.2 m. An uncertainty for this particular value has not been quoted, but we judge from other uncertainties that they have quoted [6] and from our experience with extrapolations from 0.4 m to infinite dilution, that the uncertainty in this value is probably between ± 5 and ± 10 J K^{-1} mol^{-1}. We compare this reported $C_{p,2}^0$ for ammonium propionate with our $C_{p,2}^0$ for sodium propionate by making use of previously selected [7] conventional (based on $C_{p,2}^0 = 0$ for aqueous H$^+$) ionic heat capacities. In this way we find that our $C_{p,2}^0$ for sodium propionate leads to a conventional $C_{p,2}^0 = 103$ J^{-1} K^{-1} mol^{-1} for propionate ion, while the $C_{p,2}^0$ from Cabani et al. [6] for ammonium propionate leads to $C_{p,2}^0 = 100$ J K^{-1} mol^{-1} for propionate ion.

We suggest that our $C_{p,2}^0 = C_{p,\phi}^0 = 145.6 \pm 3$ J K^{-1} mol^{-1} is probably the best available standard-state partial molar heat capacity for aqueous sodium propionate at 298.15 K.

We know of only two values of V_2^0 for aqueous sodium propionate to compare with our value. Watson and Felsing [8] made pycnometric measurements on solutions ranging from 0.3 to 2.0 M, with results that led to $V_2^0 = 52.8$ cm^3 mol^{-1}. This value was based on a linear extrapolation of V_ϕ versus $c^{1/2}$, using a slope $dV_\phi/d(c)^{1/2} = 2.70$ cm^3 mol$^{-3/2}$ l$^{1/2}$ that is considerably larger than the now reliably known Debye–Hückel limiting slope, which means that the reported value is too small in comparison with the "true" value that should be obtained from these results. We also have a reported $V_2^0 = 52.7$ cm^3 mol^{-1} based on density measurements by Hamann and Lim [9]. For reasons similar to those stated above, it is likely that this value is also too small in relation to the "true" value. On the basis of our considerations of these two previously reported [8,9] values of V_2^0, and our estimate of the uncertainty in our value, we now suggest that there is probably no significant discrepancy between the three values and also suggest that our $V_2^0 = 53.4 \pm 0.6$ cm^3 mol^{-1} is probably the best available standard-state partial molar volume for aqueous sodium propionate at 298.15 K.

ACKNOWLEDGMENT

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