Heat Capacities of Aqueous Solutions of Glutaric and Malonic Acids*

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Using a calorimeter composed of a Dewar vessel and a Beckmann thermometer, the specific heat capacities of aqueous solutions of glutaric and malonic acids were measured at 30 °C. Techniques for establishing the temperature gadient between the solution in the Dewar and the outer air bath were adopted. The partial molar heat capacities at infinite dilution were estimated assuming a relation of the form $m\phi_{Cp}=bm+cm^2$. The contributions of the $-CH_2-$ and $-COOH$ groups to the partial molar heat capacities in aqueous solution are roughly additive: for $-CH_2-$ a positive contribution and for $-COOH$ a negative one. The $\Delta(=\overline{Cp}_2{}^\circ-Cp_2(\text{pure state}))$ were also calculated and positive and negative values were obtained for $\Delta(-CH_2-)$ and $\Delta(-COOH)$, respectively.

It is widely recognized that the heat capacity of a solution is one of the essential quantities which characterizes the solute in solution, especially for solutes containing both hydrophobic and hydrophilic groups.[1–4] From this point of view, the determination of the heat capacities of an aqueous solution of 1,2-ethanediol, 1,2-propanediol, and 1,3-butanediol at 30 °C has been reported.[5]

The present study deals with similar work on aqueous solutions of glutaric and malonic acids using a laboratory-constructed calorimeter composed of a Dewar vessel and a Beckmann thermometer. The heat capacities of aqueous solutions of monocarboxylic acids and their sodium salts have been reported many years ago with sufficient precision,[6] but the situation is completely different for the dicarboxylic series.

Experimental

The calorimeter vessel used is shown in Fig. 1. Although the experimental procedures for determining the heat capacities of solutions are essentially the same as reported previously,[5] the following should be mentioned regarding the calorimeter and the manipulations in the present study. 1) The entire Dewar, except for the upper part of the stirrer and the Beckmann thermometer, is placed in a constant-temperature air bath, while in a previous work,[5] the Dewar was immersed up to the neck in a water bath. 2) In order to obtain more favorable adiabatic conditions, a magnetic stirring system was used in the Dewar. The rotational speed of the stirrer is slow but no heat conduction delay due to the viscosity of the solution was observed. 3) The temperature of the air bath was maintained at a temperature lower than that of the solution in the Dewar. This latter temperature was set near 30 °C and thus the temperature gradient between the solution in the Dewar and the air bath was established. Preliminary experiments showed that with the air bath maintained at 28 °C the most satisfactory results, *i.e.* the temperature variations as a function of time for the solution in the calorimeter before and after the heating are nearly "parallel" to each other (see Fig. 2), are obtained.

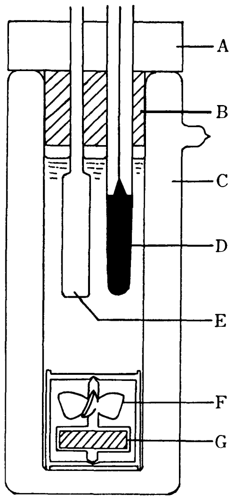

Fig. 1. Calorimeter.
A: Wood plate, B: cork cap,
C: Dewar vessel, D: Beckmann thermometer,
E: glass tube containing heater(manganin wire),
F: glass stirrer,
G: stirring magnet driven externally.

The contact between the cork cap and the Dewar was not so tight as to prevent the passage of vapor from the solution. Other parts of the experimental equipment, such as the electric heating circuit, the circuit for the measurement of the supplied electric power, and the details of the manipulations for determining the heat capacities of the solutions are the same as reported previously.[5]

The heat capacities of the Dewar determined using 100 ml of water are 24.8 cal/K (1 cal=4.184 J) and the reproducibility relative to this value was within ±2.5%. Therefore, the errors due to this uncertainty are *ca.* 0.5% for measurements of 100 g solutions. The precision of the experiments using this calorimeter was checked with the aid of an aqueous solution of Na_2CO_3 at 30 °C, the results being as shown in

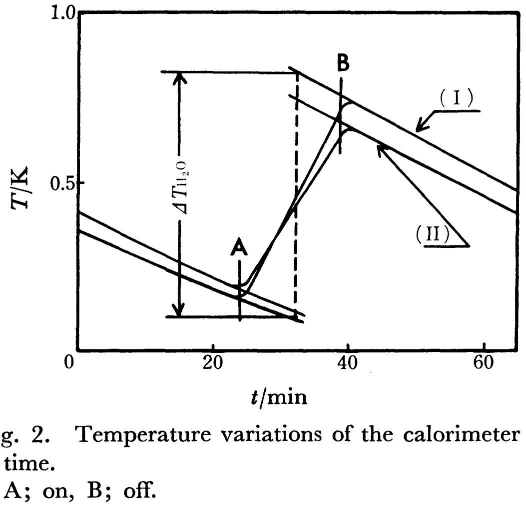

Fig. 2. Temperature variations of the calorimeter with time.
A; on, B; off.
(I); H_2O, (II); Na_2CO_3 15 wt%.

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* Heat Capacities of Aqueous Solutions. II.

TABLE 1. SPECIFIC HEAT CAPACITIES OF AQUEOUS Na_2CO_3 SOLUTIONS AT 30 °C

Concentration (wt%)	*Cp* (This work) (cal/g K)	*Cp* (Literature)[a] (cal/g K)	Ratio
15.26	0.867	0.8835	0.981
14.86	0.874	0.8855	0.987
9.48	0.900	0.9138	0.985
5.64	0.932	0.9445	0.987
5.46	0.941	0.9462	0.994
3.14	0.967	0.9685	0.998

a) Estimated from the data in "Kagaku Binran," Maruzen, Tokyo (1966), p. 775.

Table 1. There was no special reason for choosing Na_2CO_3 as a standard sample, except that it is easy to handle. As shown in Table 1, the values obtained are always smaller than those found in the literature and the differences increase with concentration. These differences might arise from differences in the degree of vaporization in pure water and that in the aqueous solution.

On taking account of the uncertainty of the heat capacity relative to the Dewar, and the deviations shown in Table 1, in order to determine the specific heat capacity within a precision of 1%, the use of the present calorimeter should be limited to solutions whose specific heat capacities exceed *ca.* 0.9 cal/g K.

Guaranteed pure-grade reagents were used without further purification.

Results and Discussion

The values of the specific heat capacities of the solutions *Cp* are listed in Tables 2 and 3. The quantity which is of greatest importance in the discussion of the solute-solvent interaction in solution is the partial molar heat capacity, which is defined as

$$\phi_{Cp} = \frac{1}{m}\{(1000+mM_2)Cp-1000Cp_1\}, \qquad (1)$$

where M_2 is the molar mass of the dissolved solute, m the molality, and the subscript 1 refers to the solvent. The limiting partial molar heat capacities, $\phi^\circ_{Cp}=\overline{Cp}^\circ_2$, can be estimated by extrapolating the relationship between ϕ_{Cp} and m. Carboxylic acids are electrolytes but the variation of the ϕ_{Cp} for the carboxylic acids with concentration is linear.[6)] Hence $\overline{Cp}^\circ_2$ was obtained from least-squares calculation of the relation

$$m\phi_{Cp} = bm+cm^2, \qquad (2)$$

on taking account of the uncertainties of the *Cp* data which increase as the concentration becomes more dilute. The relation between $m\phi_{Cp}$ and m is shown in Fig. 3. The coefficients b and c obtained are, for glutaric acid, $b=37.2\pm4.6$ and $c=17.8\pm4.0$, and for malonic acid, $b=0.2\pm3.4$ and $c=18.8\pm2.4$. In Table 4 are summarized the values of $\overline{Cp}^\circ_2(=b)$ thus obtained, along with the results reported by Ackermann *et al.*[6,7)] Table 4 also includes the values of $\Delta=\overline{Cp}^\circ_2-Cp_2$(pure state), which are considered to represent the degree of structural change caused by the dissolution of the solutes.

TABLE 2. SPECIFIC HEAT CAPACITIES OF AQUEOUS MALONIC ACID SOLUTIONS AT 30 °C

Concentration (mol/kg)	*Cp* (cal/g K)	Concentration (mol/kg)	*Cp* (cal/g K)
1.715	0.898	0.5141	0.952
1.696	0.896	0.5065	0.956
1.069	0.916	0.4008	0.968
1.065	0.909	0.2972	0.975
0.7787	0.933	0.2936	0.973
0.6127	0.949		

TABLE 3. SPECIFIC HEAT CAPACITIES OF AQUEOUS GLUTARIC ACID SOLUTIONS AT 30 °C

Concentration (mol/kg)	*Cp* (cal/g K)	Concentration (mol/kg)	*Cp* (cal/g K)
1.337	0.918	0.8412	0.933
1.335	0.914	0.8403	0.942
1.324	0.919	0.7029	0.942
1.252	0.923	0.6119	0.949
1.229	0.914	0.5040	0.961
1.193	0.933	0.4755	0.955
1.129	0.926	0.3991	0.963
1.106	0.921	0.3978	0.966
1.032	0.937	0.3173	0.975
0.9326	0.930	0.3138	0.977
0.8479	0.940	0.2331	0.983

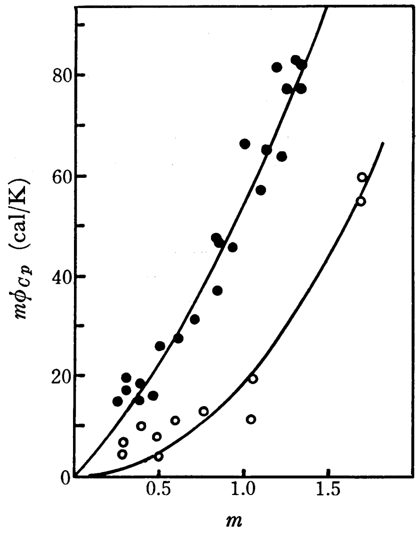

Fig. 3. Relation between apparent molar heat capacities and concentration.
●: Glutaric acid, $m\phi_{Cp}=37.2m+17.8m^2$.
○: Malonic acid, $m\phi_{Cp}=0.2m+18.8m^2$.

From the data shown in Table 4, the contribution of the $-CH_2-$ and $-COOH$ groups to the $\overline{Cp}^\circ_2$ values can be evaluated;

for $-CH_2-$,

$$1/2\{(CH_2)_3(COOH)_2-CH_2(COOH)_2\} = 18.5$$

monocarboxylc acids: 16.7—20.5

and for $-COOH$,

$$(CH_2)_3(COOH)_2-n\text{-}C_3H_7COOH = -38.3$$

$$CH_2(COOH)_2-CH_3COOH = -41.8.$$

Table 4. Partial molar heat capacities of aqueous solutions of mono- and dicarboxylic acids

Molecule	Cp_2- (pure state) (cal/mol K)	$\overline{Cp}_2^\circ$ (cal/mol K)	Δ (cal/mol K)
$(CH_2)_3(COOH)_2$	39.5[a]	37.2±4.6	−2.3
$CH_2(COOH)_2$	28.6[a]	0.2±3.4	−28.4
HCOOH	23.7[b]	21.5[b]	−2.2
CH_3COOH	29.5[b]	42.0[b]	12.5
C_2H_5COOH	38.1[b]	58.8[b]	20.7
n-C_3H_7COOH	45.3[b]	75.5[b]	30.2

a) "International Critical Tables," Vol. 5, McGraw-Hill, New York (1928), p. 102. b) Cited in Ref. 7.

The values of $\overline{Cp}_2^\circ(-CH_2-)$ for an aqueous system obtained in the present work are compatible with those reported previously,[5] (14.9—20.9 cal/mol K) from diols. The $\overline{Cp}_2^\circ(-CH_2-)$ values have been determined for carboxylic acids by Ackermann *et al.*[6,7] and Konicek and Wadsö[8] (20.1), for amines[8] (21.5), for *N*-substituted amines[8] (20.6), for alcohols[9] (22.7), for *n*-alkylamine hydrobromide[3] (21.1), for bolaform electrolytes[10] (19.4—23.7), and for alkyl-substituted ammonium chlorides[4] (12—18).

Similar calculations for Δ result in the following values:

for $-CH_2-$,

$$1/2\{(CH_2)_3(COOH)_2 - CH_2(COOH)_2\} = 13.1$$

monocarboxylic acids: 8.2—14.4

and for $-COOH$,

$$(CH_2)_3(COOH)_2 - n\text{-}C_3H_7COOH = -32.5$$

$$CH_2(COOH)_2 - CH_3COOH = -40.9.$$

In Ref. 5, 8.1 and −1.6 cal/mol K were reported for $\Delta(-CH_2-)$ and $\Delta(-OH)$, respectively. As mentioned above, Δ is a measure of the structural change accompanying the dissolution of a solute and positive values of $\Delta(-CH_2-)$ have been ascribed to the hydrophobic interaction between water and the $-CH_2-$ group, or iceberg formation.

While the values of ϕ_V°, the apparent molar volume, appear to be precise to within ±0.05 cm^3/mol or better at all temperatures, the situation is quite unfavorable for $\phi_{C_p}^\circ$. For instance, Ackermann *et al.*[7] have given, for $MeNH_3Cl$ and $EtNH_3Cl$, −2.0 and 14.6 cal/mol K, respectively, at 25 °C, while Desnoyers *et al.*[10] have reported, for the corresponding bromides, 1.9 and 24.3 cal/mol K, respectively. These differences are too large even after taking account of the difference between $\phi_{C_p}^\circ(Cl^-)$ and $\phi_{C_p}^\circ(Br^-)$. It is highly questionable, at least at the present stage of experimental accuracy inherent in the determination of $\overline{Cp}_2^\circ$, whether the small differences in the $\overline{Cp}_2^\circ(-CH_2-)$ and $\Delta(-CH_2-)$ observed for different homologs, and also for the same homolog, can be related to the neighboring organic groups.

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