

Crystal structure and thermochemical properties of potassium pyruvate $C_3H_3O_3K(s)$

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Abstract One important compound potassium pyruvate $C_3H_3O_3K(s)$ is synthesized and characterized by chemical analysis, elemental analysis, and X-ray crystallography. Xray single-crystal structural analysis reveals that the compound is formed by one CH₃COCOO⁻ anion and one metal cation K⁺. An obvious feature of the crystal structure of the compound is the formation of the five-membered chelate ring, and it is good for the stability of the compound in structure. The lattice potential energy of the compound and ionic volume of the anion CH₃COCOO⁻ are obtained from crystallographic data. The lattice potential energy is determined to be: $U_{\text{POT}}[C_3H_3O_3K(s)] = 567.7 \text{ kJ mol}^{-1}$. The V_{-} (the volume of the anion CH₃COCOO⁻) is estimated to be 0.088 nm³. Molar enthalpies of dissolution of the compound at various molalities in the double-distilled water are measured by use of an isoperibol solution-reaction calorimeter at 298.15 K. According to Pitzer's electrolyte solution theory, molar enthalpy of dissolution of C₃H₃O₃K(s) at infinite dilution is derived to be 22.9 kJ mol^{-1} . The values of relative apparent molar enthalpies (${}^{\Phi}L$), relative partial molar enthalpies (\bar{L}_2) of the compound, and relative partial molar enthalpies (\bar{L}_1) of the solvent (water) at different concentrations $m/(\text{mol kg}^{-1})$ are derived from the experimental values of the enthalpies

of dissolution of the compound. Finally, the molar enthalpy of hydration of the anion $CH_3COCOO^-(g)$ is calculated to be $-227.8 \text{ kJ mol}^{-1}$ by the design of the thermochemical cycle.

Keywords Potassium pyruvate \cdot Crystal structure \cdot Pitzer theory \cdot Molar enthalpy of dissolution at infinite dilution \cdot Enthalpy of hydration

Introduction

Pyruvic acid CH₃COCOOH is one of the basic metabolic intermediates involved in the whole organisms. In the common food sources of animal and plant, the carbohydrate is used most commonly. The carbohydrate undergoes a series of biochemical reactions and finally broken down to pyruvate as one of the most important products in the biological body, others including lactic acid, amino acids, etc. This is regarded as the most effective way to gain energy and carbon sources. In addition, the alanine as one of important amino acids in biological body can be directly generated from pyruvic acid because it can be combined with amino transfer reaction. Therefore, it also plays an important role in nitrogen metabolism. In addition, it can react with CoA to form acetyl-CoA and also has an important relationship with the fatty acid metabolism.

Pyruvic acid is an important organic acid and has a wide usage. It can easily be dissociated to produce the pyruvate anion in the weak basic solution of biological body. The physiological functions of pyruvate are as follows: mass reduction, increasing muscular endurance and physical performance, antioxidation, reducing the blood fat and cholesterin, protecting cardiac muscle and so on. Pyruvate is widely used in the development and production of

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functional food, biochemical products, cosmetics, pesticide, etc.

Pyruvic acid and the salts it produces are widely used in medical field. They are used for the production of sedatives, antioxidants, antivirals, synthetic drugs for treating high blood pressure and so on. As for pyruvic acid [1], as new type of medicine, pesticide, and daily chemical intermediates, its market demand is growing very quickly at home and abroad. With the improvement of people's living standard, the demand of the pyruvic acid salt series products will be gradually expanded in the domestic and abroad markets, especially the application as a kind of raw material of mass-loss drug as well as the application and development of new refrigerant is very promising [2].

In this paper, the crystal structure and some important thermodynamic properties [3–7] of the compound $C_3H_3O_3K(s)$ are reported. And the lattice potential energy of the compound and ionic volume of the anion are obtained from crystallographic data. Molar enthalpies of dissolution of the compound at various molalities are measured by an isoperibol solution-reaction calorimeter at 298.15 K in the double-distilled water. According to Pitzer's theory, the molar enthalpy of dissolution of the title compound at infinite dilution is obtained. The values of relative apparent molar enthalpies (${}^{\Phi}L$), relative partial molar enthalpies (\overline{L}_2) of the compound and relative partial molar enthalpies (\overline{L}_1) of the solvent (water) at different concentrations $m/(\text{mol kg}^{-1})$ are derived from the experimental values of the enthalpies of dissolution of the compound. At last, the molar enthalpy of hydration of the anion CH₃COCOO⁻(g) is calculated.

Experimental

Synthesis of the title compound

Information on the provenances and purities of the chemicals used in the synthesis and calorimetric experiments is listed in Table 1. In the paper, the compound $C_3H_3O_3$ K(s) is synthesized by the following procedure: pyruvic acid reacts with potassium hydroxide at a mole ratio of *n* (pyruvic acid): *n* (potassium hydroxide) = 1:1 in anhydrous ethanol solution. The mixed solution is boiled under reflux for 2 h. And the mixed solution is left at room temperature. After several days, colorless single crystals are separated from the mother liquid and recrystallized with anhydrous ethanol three times. Finally, the sample with a crystal shape is placed in a vacuum desiccator to dry in vacuum for 12 h at T = 303.15 K. The final product is placed in a weighing bottle and preserved in a desiccator. The purity of the compound has been analyzed by element analyzer (model: PE-2400 II, PerkinElmer, USA), under its "CHN mode", and "O mode". The element analyzer has three modes: "CHN mode", "CHNS mode", and "O mode". We can analyze oxygen element exactly under its "O mode". The mass fraction purity of the C, H, and O are determined. For $C_3H_3O_3K(s)$, the percentage of the K is calculated and the values (analysis, calculated for C₃H₃ O₃K(s): C 28.56, H 2.40, O 38.05, K 30.99 %; found: C 28.57, H 2.41, O 38.06, K 30.96 %) show that the mass fraction purity of the compound is >0.996.

X-ray crystallography

A crystal with dimensions of 0.47 mm \times 0.40 mm \times 0.20 mm is glued to the fine glass fiber and then mounted on the Bruker Smart-1000 CCD diffractometer with Mo–K α radiation, $\lambda = 0.071073$ nm. The intensity data are collected in the $\varphi - \omega$ scan mode at $T = (298 \pm 2)$ K. The empirical absorption corrections are based on multi-scan. The structure is solved by direct method and difference Fourier synthesis, and all non-hydrogen atoms are refined anisotropically on F^2 by full-matrix leastsquares method. All calculations are performed with the program package SHELXTL [8, 9].

We have applied for the CCDC number 1035339 for the compound $C_3H_3O_3K(s)$.

Isoperibol solution-reaction calorimeter

The isoperibol solution-reaction calorimeter consists primarily of a precision temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precise temperature measuring system, and a data acquisition and processing system.

Table 1 Information on the provenances and purities of the chemicals used in the synthesis and calorimetric experiments

Chemicals	Provenances	Mass fraction purity
Pyruvic acid	J&K Scientific Ltd. China	>0.99
Potassium hydroxide	J&K Scientific Ltd. China	>0.999
Anhydrous ethyl alcohol	Tianjin No. 3 Chemical Reagent Factory. China	0.995
Potassium pyruvate	Prepared by our laboratory	>0.99
Potassium chloride	J&K Scientific Ltd. China	>0.999

During whole experiments, the water thermostat is automatically maintained at T = 298.15 K and the maximum variation is found to be $\pm 1 \times 10^{-3}$ K. The platinum resistance thermometer is used to measure the temperature of the calorimetric chamber in the whole dissolution experiment, and it has a high precision of ± 0.001 K. Experiments have demonstrated that the precision of measuring the temperature can reach $\pm 1 \times 10^{-4}$ K. The principle and structure of the calorimeter are described in detail elsewhere [10].

The reliability of the calorimeter is verified previously by measuring the molar enthalpy of dissolution of KCl (calorimetrically primary standard) in the double-distilled water. According to the molar ratio of KCl to water, $n_{\rm KCl}: n_{\rm H_2O} \approx 1:1110$, a certain amount of KCl is dissolved in 100 cm³ of the double-distilled water at $T = (298.15 \pm 0.001)$ K. The average molar enthalpy of dissolution of KCl is $(17,547 \pm 13)$ J mol⁻¹, which compares with corresponding published data $(17,536 \pm 3.4)$ J mol⁻¹ under the same experimental condition [10]. Experiments demonstrate that the uncertainty between the measuring value and the literature value is within ± 0.3 %.

Results and discussion

Description of crystal structure

The crystal data and structure refinement for the compound are summarized in Table 2. The selected bond lengths and angles of the title compound are listed in Table 3. Table 2 shows that the crystal system of $C_3H_3O_3K(s)$ is monoclinic, the space group is P2(1), unit cell dimensions are a = 0.40118(4) nm, b = 0.58401(7) nm, c = 2.2074(2)nm, $\alpha = \gamma = 90^{\circ}$, $\beta = 91.0270(10)^{\circ}$, and Z = 4. The calculated density of $C_3H_3O_3K(s)$ is 1.620 g cm⁻³, and the volume of formula unit is 0.51709(9) nm³. The molecular structure of each C₃H₃O₃K(s) includes one CH₃COCOO⁻ anion and one K⁺ cation. Each of K⁺ cation connects with the keto oxygen and the carboxylate oxygen at the same time. The five-membered chelate ring is formed by the coordination of O atoms of carboxylate and keto form with K⁺ cation, and the chelate coordination structure is good for the reduction of the energy and the structural stability of the compound from the viewpoint of energy. These three atoms form a chelate ring together with other two carbon atoms. The structure of the molecule of the compound can be seen from Fig. 1, and the stacking crystal structure of the compound in unit cell is shown in Fig. 2.

For $C_3H_3O_3K(s)$, single crystal X-ray analysis reveals that in the whole crystal structure, the five $CH_3COCOO^$ anions are six-coordinated to one K^+ cation by two oxygen atoms (O1and O3) of one pyruvate group, two oxygen

Table 2 Summary of crystallographic data and refinement parameters for $C_3H_3O_3K(s)$

Empirical formula	$C_3H_3O_3K(s)$
Formula weight	126.15
Temperature/K	298 ± 2
Wavelength/nm	0.071073
Crystal system	Monoclinic
Space group	P2(1)
<i>a</i> /nm	0.40118(4)
<i>b</i> /nm	0.58401(7)
c/nm	2.2074(2)
α/°	90
βI°	91.0270(10)
$\gamma / ^{\circ}$	90
V/nm ³	0.51709(9)
Ζ	4
Calculated density/(g cm^{-3})	1.620
Absorption coefficient/mm ⁻¹	0.916
F(000)	256
Crystal size/mm ³	$0.42 \times 0.42 \times 0.33$
Theta range for data collection/°	3.61 to25.00
Limiting indices	$-4 \le h \le 4$
	$-4 \le k \le 6$
	$-25 \le 1 \le 26$
Reflections collected/unique	2379/905
	[R(int) = 0.0517]
Completeness to θ 25.02	99.2
Absorption correction	Semiempirical from equivalents
Refinement method	0.7520 and 0.6997
Data/restraints/parameters	Full-matrix least-squares on F2
Goodness of fit on F2	905/0/65
Final <i>R</i> indices $[I > 2 \text{sigma}(I)]$	1.194
R indices (all data)	R1 = 0.0497
	wR2 = 0.1291
Extinction coefficient	R1 = 0.0549
	wR2 = 0.1319
Largest diff. peak and hole/ (e nm ⁻³)	420 and -407

atoms (O2) from two pyruvate groups, and two oxygen atoms (O1) from other two pyruvate groups (see Fig. 2). The coordination mode of octahedral pattern around the central K^+ is formed.

The distances (Table 3) of oxygen atoms to the metal cation are lying in the range 0.2694(3)–0.3296(3) nm for $C_3H_3O_3$ -K(s). The C–C bonds are found to have lengths 0.1554(5) and 0.1490(6) nm. The C–O bonds (C1–O1 and C1–O2) in the carboxylate group are found to have lengths 0.1248(4) and 0.1243(4) nm, respectively. The C–O bonds (C2–O3) in the keto group are found to have lengths 0.1208(5) nm. The angles

Table 3 Selected bond lengths (nm) and bond angles (deg) for $C_3H_3O_3K(s)$

Bonds	Bond length/nm	Bonds	Bond angle/°
K(1)–O(2)#1	0.2694(3)	O(2)#1-K(1)-K(1)#5	135.46(7)
K(1)-O(1)#2	0.2718(3)	O(1)#2-K(1)-K(1)#5	137.43(6)
K(1)–O(1)	0.2724(3)	O(1)-K(1)-K(1)#5	42.46(6)
K(1)-O(1)#3	0.2760(3)	O(1)#3-K(1)-K(1)#5	83.75(6)
K(1)-O(2)#4	0.2819(3)	O(2)#4-K(1)-K(1)#5	42.09(6)
K(1)–O(3)	0.2853(3)	O(3)-K(1)-K(1)#5	78.74(8)
K(1)-O(2)#3	0.3190(3)	O(2)#3-K(1)-K(1)#5	86.08(6)
K(1)-C(1)#3	0.3296(4)	C(1)#3-K(1)-K(1)#5)	81.82(6)
O(1)–C(1)	0.1248(4)	K(1)#2-K(1)-K(1)#5	180.0
O(1)-K(1)#5	0.2718(3)	O(2)#1-K(1)-K(1)#9	106.93(8)
O(1)-K(1)#6	0.2760(3)	O(1)#2-K(1)-K(1)#9	40.34(6)
O(2)–C(1)	0.1243(4)	O(1)-K(1)-K(1)#9	80.58(6)
O(2)-K(1)#7	0.2694(3)	O(1)#3-K(1)-K(1)#9	76.97(6)
O(2)-K(1)#8	0.2819(3)	O(2)#4-K(1)-K(1)#9	148.77(7)
O(2)-K(1)#6	0.3190(3)	O(3)-K(1)-K(1)#9	100.63(8)
O(3)–C(2)	0.1208(5)	O(2)#3-K(1)-K(1)#9	39.91(5)
C(1)–C(2)	0.1554(5)	C(1)#3-K(1)-K(1)#9	59.30(7)
C(1)-K(1)#6	0.3296(4)	K(1)#2-K(1)-K(1)#9	66.09(2)
C(2)–C(3)	0.1490(6)	K(1)#5-K(1)-K(1)#9	113.91(2)
C(3)-H(3A)	0.09600	O(2)#1-K(1)-K(1)#10	49.45(7)
C(3)-H(3B)	0.09600	O(1)#2-K(1)-K(1)#10	100.29(7)
C(3)-H(3C)	0.09600	O(1)-K(1)-K(1)#10	140.82(6)
O(2)#1-K(1)-O(1)#2	8.603(9)	O(1)#3-K(1)-K(1)#10	39.61(6)
O(2)#1-K(1)-O(1)	16.868(10)	O(2)#4-K(1)-K(1)#10	87.45(6)
O(1)#2-K(1)-O(1)	9.497(9)	O(3)-K(1)-K(1)#10	160.35(7)
O(2)#1-K(1)-O(1)#3	8.891(9)	O(2)#3-K(1)-K(1)#10	73.22(6)
O(1)#2-K(1)-O(1)#3	11.0.83(6)	C(1)#3-K(1)-K(1)#10	56.75(7)
O(1)-K(1)-O(1)#3	1.0121(6)	K(1)#2-K(1)-K(1)#10	66.09(2)
O(2)#1-K(1)-O(2)#4	9.337(9)	K(1)#5-K(1)-K(1)#10	113.91(2)
O(1)#2-K(1)-O(2)#4	16.910(9)	K(1)#9-K(1)-K(1)#10	88.13(3)
O(1)-K(1)-O(2)#4	8.351(9)	C(1)-O(1)-K(1)#5	130.0(2)
O(1)#3-K(1)-O(2)#4	8.003(9)	C(1)–O(1)–K(1)	116.3(2)
O(2)#1-K(1)-O(3)	11.093(10)	K(1)#5–O(1)–K(1)	94.97(9)
O(1)#2-K(1)-O(3)	7.648(11)	C(1)-O(1)-K(1)#6	104.1(2)
O(1)-K(1)-O(3)	5.862(8)	K(1)#5-O(1)-K(1)#6	100.05(8)
O(1)#3-K(1)-O(3)	15.961(10)	K(1)-O(1)-K(1)#6	109.54(10)
O(2)#4-K(1)-O(3)	9.364(11)	C(1)-O(2)-K(1)#7	146.1(3)
O(2)#1-K(1)-O(2)#3	11.701(7)	C(1)-O(2)-K(1)#8	120.4(3)
O(1)#2-K(1)-O(2)#3	8.012(8)	K(1)#7-O(2)-K(1)#8	93.37(9)
O(1)-K(1)-O(2)#3	7.422(8)	C(1)-O(2)-K(1)#6	83.8(2)
O(1)#3-K(1)-O(2)#3	4.325(8)	K(1)#7–O(2)-K(1)#6	90.65(9)
O(2)#4-K(1)-O(2)#3	10.967(7)	K(1)#8-O(2)-K(1)#6	96.21(10)
O(3)-K(1)-O(2)#3	12.429(9)	C(2)–O(3)–K(1)	116.5(2)
O(2)#1-K(1)-C(1)#3	10.539(10)	O(2)–C(1)–O(1)	126.9(4)
O(1)#2-K(1)-C(1)#3	9.772(9)	O(2)-C(1)-C(2)	116.4(3)
O(1)-K(1)-C(1)#3	8.567(9)	O(1)-C(1)-C(2)	116.6(3)
O(1)#3-K(1)-C(1)#3	2.155(8)	O(2)-C(1)-K(1)#6	74.2(2)
O(2)#4-K(1)-C(1)#3	9.293(9)	O(1)-C(1)-K(1)#6	54.31(18)

Table 5 continued	Table	3	continue	d
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Bonds	Bond length/nm	Bonds	Bond angle/°
O(3)-K(1)-C(1)#3	14.258(9)	C(2)–C(1)–K(1)#6	161.5(2)
O(2)#3-K(1)-C(1)#3	2.202(8)	O(3)–C(2)–C(3)	122.5(4)
O(2)#1-K(1)-K(1)#2	4.454(7)	O(3)–C(2)–C(1)	119.2(3)
O(1)#2-K(1)-K(1)#2	4.257(6)	C(3)-C(2)-C(1)	118.3(4)
O(1)-K(1)-K(1)#2	13.754(6)	C(2)-C(3)-H(3A)	109.5
O(1)#3-K(1)-K(1)#2	9.625(6)	C(2)–C(3)–H(3B)	109.5
O(2)#4-K(1)-K(1)#2	13.791(6)	H(3A)-C(3)-H(3B)	109.5
O(3)-K(1)-K(1)#2	10.126(8)	C(2)-C(3)-H(3C)	109.5
O(2)#3-K(1)-K(1)#2	9.392(6)	H(3A)-C(3)-H(3C)	109.5
C(1)#3-K(1)-K(1)#2	9.818(6)	H(3B)-C(3)-H(3C)	109.5

Symmetry code: #1 x + 1, y - 1, z; #2x + 1, y, z; #3 - x + 1/2, y - 1/2, -z + 1/2; #4 x, y - 1, z; #5 x - 1, y, z; #6 -x + 1/2, y + 1/2, -z + 1/2; #7 x - 1, y + 1, z; #8 x, y + 1, z; #9 -x + 3/2, y + 1/2, -z + 1/2; #10 -x + 3/2, y - 1/2, -z + 1/2



Fig. 1 Molecular structure of potassium pyruvate C₃H₃O₃K(s)

O1-C1-C2, O2-C1-C2, and O3-C2-C1 are 116.6(3)°, 116.4(3)°, and 119.2(3)° (see Table 3).

For $C_3H_3O_3K(s)$, there are no hydrogen bonds existing in the whole crystal structure, and the stacking of the structure is completed mainly by the electrostatic force, weak coordination bond and Van der Waals interaction force.

Lattice potential energy of the compound and ionic volume of pyruvate anion

Equation (1) used to estimate lattice potential energy of general type of salt M_pX_q is obtained from the literature [11]:

$$U_{\rm POT} = \sum n_i z_i^2 \left(\alpha' / V_{\rm m}^{1/3} + \beta' \right) \tag{1}$$

where α' and β' are appropriate fitted coefficients chosen according to the stoichiometry of the salt, n_i is the number of ion with a charge z_i in the formula unit, and V_m is the molecular volume.

For the salts MX(1:1), MX₂(1:2), and M₂X (2:1), the Eq. (1) is changed to:

$$U_{\rm POT} = |z_+||z_-|v(\alpha'/V_{\rm m}^{1/3} + \beta')$$
(2)

where z_+ and z_- are the respective charges on the cation and anion of the compound, and v is the number of ions per molecule and equals (p + q). In the case of the salt of formula MX with charge ratio (1:1) like potassium pyruvate, $z_+ = 1$, $z_- = 1$, p = 1, q = 1, v = 2, $\alpha' = 117.3$ kJ mol⁻¹·nm, $\beta' = 51.9$ kJ mol⁻¹ [12], and $V_{\rm m}$ is in unit of nm³ and expressed as follows [11]:

$$V_{\rm m} = M_{\rm m}/\rho N_{\rm A} = 1.66045 \times 10^{-3} M_{\rm m}/\rho \tag{3}$$

where $N_{\rm A}$ is Avogadro's constant, 6.02245×10^{23} molecule·mol⁻¹, $M_{\rm m}$ is molar weight of the molecule, ρ is the density of the substance, and $V_{\rm m}$ (MX) is calculated to be 0.1038 nm³ from the formula (3), consequently. Thus, the Eq. (2) is changed to [11]:

$$U_{\rm POT} = \gamma (\rho/M_{\rm m})^{1/3} + \delta \tag{4}$$

where the values of the constants for MX (1:1) are: $\gamma = 1981.2 \text{ kJ mol}^{-1} \cdot \text{cm}$ and $\delta = 103.8 \text{ kJ mol}^{-1}$. Lattice potential energy of the compound C₃H₃O₃K(s) is determined to be $U_{\text{POT}} = 567.7 \text{ kJ mol}^{-1}$, which reveals that the structure of the compound is stable based on the larger lattice potential energy.

In addition, for a salt of molecular formula $M_p X_q$,

$$V_m(\mathbf{M}_p \mathbf{X}_q) = pV_+ + qV_- \tag{5}$$

where V_{-} and V_{+} are the volumes of the anion and cation, p = 1 and q = 1 for C₃H₃O₃K(s). V_{K+} is 0.0277 nm³





according to the literature [13], the V_- (the volume of the anion CH₃COCOO⁻) is estimated to be 0.088 nm³.

Molar enthalpy of dissolution at infinite dilution and Pitzer's parameters

The title compound is soluble in the double-distilled water. The experimental values of molar enthalpies of dissolution $(\Delta_s H_m)$ of the title compound in the double-distilled water are given in Table 4, and the curvilinear relationship of $\Delta_s H_m$ /(kJ mol⁻¹) with molalities *m*/(mol kg⁻¹) is shown in Fig. 3.

The molar enthalpy of dissolution of the compound $(\Delta_s H_m)$ in the double-distilled water is expressed as [14]:

$$\Delta_s H_m = \Delta_s H_m^\infty + {}^{\Phi}L \tag{6}$$

in which $\Delta_{\rm s} H_{\rm m}^{\infty}$ is the molar enthalpy of dissolution at infinite dilution, ${}^{\Phi}L$ is the apparent relative molar enthalpy. For the salts of MX (1:1), according to Pitzer's electrolyte solution theory, the apparent relative molar enthalpy ${}^{\Phi}L$ may be expressed as:

$${}^{\Phi}L = v |z_{M}z_{X}|A_{H} \ln(1 + bI^{1/2})/2b - 2v_{M}v_{X}RT^{2}[m\beta_{MX}^{(0)L} + my'\beta_{MX}^{(1)L} + (v_{M}v_{X})^{1/2}m^{2}C_{MX}^{\Phi L}/2]$$
(7)

where *I* is ionic strength, $(\sum m_i z_i^2/2)$, $\beta_{MX}^{(0)L}$, $\beta_{MX}^{(1)L}$, and $C_{MX}^{\Phi_L}$ are Pitzer's parameters for enthalpies, the coefficients $\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$ account for various types of short-range interactions between M and X, and for indirect forces arising from the solvent, and the third coefficient $C_{MX}^{\Phi_L}$ represents for triple ion interactions and is important only at high concentrations or with strong triple ion interaction. In this paper, $C_{MX}^{\Phi_L}$ may not be overlooked for the compound $C_3H_3O_3K(s)$ because formation and breaking of the fivemembered chelate ring of the [CH₃COCOO]⁻ anion with K⁺ cation are similar to the three-ion interaction. v is the total number of ions formed from the salt ($v = v_{\rm M} + v_{\rm X}$). $z_{\rm M}$ and $z_{\rm X}$ are the respective charges on the cation and anion of the compound. b is a parameter with the value 1.2 kg^{1/2}mol^{-1/2} for all solutions. $y' = 2[1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})]/\alpha^2 I$ and $\alpha = 2.0$ kg^{1/2} mol^{-1/2}. $m/(\text{mol kg}^{-1})$ is the molality of the compound in the solution. R is molar gas constant, 8.3145 J K⁻¹ mol⁻¹. $A_{\rm H}$ is Debye–Huckel parameter for enthalpy [14], $A_{\rm H} = 1986$ J mol⁻¹ at T = 298.150 K.

For the case of salt of the formula MX with charge ratio (1:1) such as $C_3H_3O_3K(s)$, the apparent relative molar enthalpy ${}^{\Phi}L$ for it may be expressed as: [15]

$${}^{\mathbf{b}}L = 2(A_{\rm H}/2.4)\ln(1+1.2I^{1/2}) - 2RT^{2}[m(\beta_{\rm MX}^{(0)\rm L} + y'\beta_{\rm MX}^{(1)\rm L}) + m^{2}C_{\rm MX}^{^{0}\rm L}/2]$$
(8)

From above equations, the working equation to determine Pitzer parameters is shown as:

$$Y = [\Delta_{\rm s} H_{\rm m} - A_{\rm H} \ln(1 + 1.2I^{1/2})/1.2]/(2RT^2)$$

= $\alpha_0 - m\beta_{\rm MX}^{(0)L} - my'\beta_{\rm MX}^{(1)L} - m^2 C_{\rm MX}^{\Phi_L}/2$ (9)

where *Y* is the extrapolation function and $\alpha_0 = \Delta_s H_m^{\infty}/(2RT^2)$. Regression of *Y* against -m, -my', and $-0.5 m^2$ is made by least squares to obtain $\alpha_0 = 0.0155$, $\beta_{MX}^{(0)L} = -33.91106$, $\beta_{MX}^{(1)L} = 37.93714$ and $C_{MX}^{\Phi_L} = 280.16511$ with a standard deviation of the fitting 3.13777×10^{-4} for C₃H₃O₃K(s), respectively. The molar enthalpy of dissolution for C₃H₃O₃K(s) at infinite dilution is determined to be $\Delta_s H_m^{\infty} = 22.9$ kJ mol⁻¹. The three-dimensional chart of *Y* against -m and -my' is plotted in Fig. 4.

To calculate the enthalpy of hydration of $CH_3COCOO^-(g)$, a thermochemical cycle is designed as follows (Scheme 1):

nol ⁻¹ -m/mol kg ⁻¹ -my/mol kg ⁻¹ -8.04598E-4 -7.74805E-4 -0.00159 -0.00151 -0.00239 -0.00224 -0.00318 -0.00295 -0.00318 -0.00295 -0.00365 -0.00365 -0.00477 -0.00435 -0.00635 -0.00571 -0.00635 -0.00571	-0.5 m ² mol ² kg ⁻² -3.23689E-7 -1.26811E-6 -2.85797E-6 -5.05224E-6 -7.89256E-6 -1.13638E-5 -1.54438E-5 -2.01536E-5	Y 0.01364 0.01192 0.01040 0.00964 0.00923	^{<i>Φ</i>} L/kJ mol ⁻¹ -2.69435 -5.21892 -7.44863 -8 55787	$10^{-5} \left(\partial^{\varPhi} L / \partial_{\mathrm{m}} \right)_{\mathrm{T,P}}$	$ar{L}_1$ /J mol $^{-1}$	$ar{L}_2$ /kJ mol $^{-1}$
-8.04598E-4 -7.74805E-4 -0.00159 -0.00151 -0.00239 -0.00224 -0.00318 -0.00295 -0.00318 -0.00295 -0.00365 -0.00365 -0.00435 -0.00435 -0.00635 -0.00571 -0.00635 -0.00571	-3.23689E-7 -1.26811E-6 -2.85797E-6 -5.05224E-6 -7.89256E-6 -1.13638E-5 -1.54438E-5 -2.01536E-5	0.01364 0.01192 0.01040 0.00964 0.00923 0.00823	-2.69435 -5.21892 -7.44863 -8 55787			
$\begin{array}{rcrcr} -0.00159 & -0.00151 \\ -0.00239 & -0.00224 \\ -0.00318 & -0.00295 \\ -0.00397 & -0.00365 \\ -0.00435 & -0.00435 \\ -0.00556 & -0.00633 \\ -0.00571 & -0.00571 \\ -0.00514 & -0.00639 \\ \end{array}$	-1.26811E-6 -2.85797E-6 -5.05224E-6 -7.89256E-6 -1.13638E-5 -1.54438E-5 -2.01536E-5	0.01192 0.01040 0.00964 0.00923 0.00895	-5.21892 -7.44863 -8.55787	-31.578	36.797	-2.543
$\begin{array}{rcrcrc} -0.00239 & -0.00224 \\ -0.00318 & -0.00295 \\ -0.00397 & -0.00365 \\ -0.00435 & -0.00435 \\ -0.00556 & -0.00503 \\ -0.00535 & -0.00571 \\ -0.00531 & -0.00539 \end{array}$	-2.85797E-6 -5.05224E-6 -7.89256E-6 -1.13638E-5 -1.54438E-5 -2.01536E-5	0.01040 0.00964 0.00923 0.00895	-7.44863 -8 55787	-22.852	104.325	-3.645
$\begin{array}{rcl} -0.00318 & -0.00295 \\ -0.00397 & -0.00365 \\ -0.00477 & -0.00435 \\ -0.00556 & -0.00503 \\ -0.00635 & -0.00571 \\ -0.00635 & -0.00539 \\ \end{array}$	-5.05224E-6 -7.89256E-6 -1.13638E-5 -1.54438E-5 -2.01536E-5	0.00964 0.00923 0.00895	-855787	-16.979	174.687	-4.067
$\begin{array}{rcrcr} -0.00397 & -0.00365 \\ -0.00477 & -0.00435 \\ -0.00556 & -0.00503 \\ -0.00635 & -0.00571 \\ -0.00634 & -0.00639 \\ \end{array}$	-7.89256E-6 -1.13638E-5 -1.54438E-5 -2.01536E-5	0.00923	101000	-12.713	231.223	-4.050
$\begin{array}{rcl} -0.00477 & -0.00435 \\ -0.00556 & -0.00503 \\ -0.00635 & -0.00571 \\ -0.00714 & -0.00639 \end{array}$	-1.13638E-5 -1.54438E-5 -2.01536E-5	0 00895	-9.14759	-9.400	267.092	-3.744
$\begin{array}{rcl} -0.00556 & -0.00503 \\ -0.00635 & -0.00571 \\ -0.00714 & -0.00639 \end{array}$	-1.54438E-5 -2.01536E-5	000000	-9.55478	-6.793	277.899	-3.248
-0.00635 $-0.00571-0.00714$ -0.00639	-2.01536E-5	0.00872	-9.88615	-4.729	262.944	-2.638
-0.00714 -0.00639		0.00854	-10.13046	-3.083	223.709	-1.968
	-2.55175E-5	0.00848	-10.22313	-1.775	163.038	-1.278
-0.00794 -0.00706	-3.15450E-5	0.00842	-10.29053	-0.752	85.355	-0.607
-0.00953 -0.00837	-4.53720E-5	0.00838	-10.33827	0.572	-93.421	0.534
-0.01111 -0.00966	-6.17049E-5	0.00834	-10.38086	1.148	-255.004	1.265
-0.01269 -0.01094	-8.05237E-5	0.00832	-10.39584	1.133	-328.540	1.428
-0.01428 -0.0122	-1.02002E-4	0.00831	-10.40005	0.633	-232.298	0.893
-0.01587 -0.01344	-1.25941E-4	0.00830	-10.41549	-0.272	123.389	-0.442
-0.01745 -0.01466	-1.52332E-4	0.00828	-10.43375	-1.518	832.440	-2.660
-0.01984 -0.01648	-1.96716E-4	0.00822	-10.49834	-3.936	2787.362	-7.818
e solute, $\Delta_s H_m$ is the molar enthalpy of dissolute e relative partial molar enthalpy of the double- is \pm 0.01 kPa; the uncertainty value of <i>m</i> is	ion of the compound, $y' = [$ distilled water; $\overline{L_2}$ is the rela \pm 0.0002 mol kg ⁻¹ ; the un	$1 - (1 + 2I^{1/2})$ tive partial m certainty valu	$\frac{\left \exp\left(-2I^{1/2}\right)\right }{2}$ olar enthalpy of te of $\Delta_{s}H_{m}$ is \pm	21, and Y is the extrapol the compound. The unc $0.3 \ \%$	ation function. ^{<i>Ф</i>} <i>L</i> certainty value of <i>T</i>	is the apparent r is ± 0.001 K,
$\begin{array}{llllllllllllllllllllllllllllllllllll$	ion of ± 0.00±	6.17049E-5 8.05237E-5 8.05237E-5 1.02002E-4 1.25941E-4 1.52332E-4 1.56716E-4 the compound, $y' = [$ d water; $\overline{L_2}$ is the relation of g^{-1} ; the unit	$6.17049E-5$ 0.00834 $8.05237E-5$ 0.00832 $1.02002E-4$ 0.00831 $1.25941E-4$ 0.00830 $1.52332E-4$ 0.00828 $1.96716E-4$ 0.00822 the compound, $y' = [1-(1+2)^{1/2}]$ the compound, $y' = [1-(1+2)^{1/2}]$ the matrix the relative partial m 002 mol kg ⁻¹ ; the uncertainty value	6.17049E-5 0.00834 -10.38086 $8.05237E-5$ 0.00832 -10.39584 $1.02002E-4$ 0.00831 -10.39584 $1.025941E-4$ 0.00830 -10.40005 $1.52332E-4$ 0.00820 -10.41549 $1.52332E-4$ 0.00828 -10.43375 $1.96716E-4$ 0.00822 -10.49337 $1.96716E-4$ 0.00822 -10.493375 $1.96716E-4$ 0.00822 -10.493375 $1.96716E-4$ 0.00822 -10.493375 0.00822 -10.403375 -10.493375 0.00822 -10.40834 -10.49834 0.00822 -10.40834 -10.49834	$6.17049E-5$ 0.00834 -10.38086 1.148 $8.05237E-5$ 0.00832 -10.39584 1.133 $1.02002E-4$ 0.00831 -10.40005 0.633 $1.25941E-4$ 0.00830 -10.41549 -0.272 $1.52332E-4$ 0.00828 -10.41549 -0.272 $1.52332E-4$ 0.00822 -10.498345 -1.518 $1.96716E-4$ 0.00822 -10.498345 -3.936 the compound, $y' = [1-(1 + 2I^{1/2})exp(-2I^{1/2})]/2I$, and Y is the extrapol dwater; $\overline{L_2}$ is the relative partial molar enthalpy of the compound. The uncompound the enthalpy of the compound. The uncompound the enthalpy of the compound. The uncompound to $\Lambda.H_{-}$ is ± 0.3 %	6.17049E-5 0.00834 -10.38086 1.148 -255.004 8.05237E-5 0.00832 -10.39584 1.133 -328.540 1.02002E-4 0.00831 -10.40005 0.633 -328.540 1.25941E-4 0.00830 -10.41549 -0.272 123.389 1.52332E-4 0.00828 -10.43375 -1.518 832.440 1.96716E-4 0.00822 -10.49834 -3.936 2787.362 the compound, $y' = [1-(1+2I^{1/2})\exp(-2I^{1/2})]/2I$, and Y is the extrapolation function. ${}^{\Phi}L$ d water; \overline{L}_{i} is the relative partial molar enthalpy of the compound. The uncertainty value of 7002 mol kg ⁻¹ ; the uncertainty value of Δ_{Hm} is ± 0.3 %



Fig. 3 Plot of the measured $\Delta_s H_m$ against molality for potassium pyruvate C₃H₃O₃K(s) at T = 298.15 K

An important formula can be obtained from the above thermochemical cycle in Scheme 1:

$$\Delta_{\rm s} H_{\rm m}^{\infty} = (U_{\rm POT} + 2RT) + (\Delta H_+ + \Delta H_-) \tag{11}$$

In the formula (11), for C₃H₃O₃K(s), it is given that $U_{\rm POT} = 567.7 \text{ kJ mol}^{-1}$, $\Delta_{\rm s} H_{\rm m}^{\infty} = 22.9 \text{ kJ mol}^{-1}$, and $\Delta H_{+} = -322 \text{ kJ mol}^{-1}$, then the molar enthalpy of hydration of the anion CH₃COCOO⁻(g) is calculated as $\Delta H_{-} = -227.8 \text{ kJ mol}^{-1}$.

Fig. 4 Three-dimensional graphics of regression of *Y* against -m and -my' for potassium pyruvate $C_3H_3O_3K(s)$ at T = 298.15 K

The quantities $\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$ are attributed to the shortrange interaction between the cation and anion. The absolute values of $\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$ are very small for an usual electrolyte and have a tendency to increase along with the volume and the quantity of the ion. It may be noted that the absolute values of $\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$ are significantly greater than those of usual electrolytes mainly since the volume of the anion is greater than that of the usual electrolyte. This shows that various types of strong short-range interactions exist between cation and anion in the solutions obtained from dissolution of the title compound. $\beta_{MX}^{(0)L}$ has a negative value, that is $(\partial \beta_{MX}^{(0)} / \partial T)_p < 0$, which indicates that the value of $\beta_{MX}^{(0)L}$ drops with the rise of the temperature. This shows that the interionic repulsive force decreases with the increase of the temperature. The third coefficient $C_{\rm MX}^{\Phi_{\rm L}}$ for triple ion interaction has a very high value in the research, it may be ascribed to the chelate behavior of the title compound in the aqueous solution, and the larger ionization energy of the electrovalent compound in water is caused mainly by the formation and destruction of the five-membered chelate rings. It can be seen from Fig. 4 that ionization or dissociation of the compound in pure water is not complete, it is a kind of the weak electrolyte rather than strong electrolyte, and a certain ionization degree or dissociation degree of counter ions emerges among the solution. The pH values of the solutions after





Scheme 1 Thermochemical cycle

dissolution are much more than 7 because the hydrolysis of $[CH_3COCOO]^-$ takes place, so there are three kinds of ions existing in the solutions, including K⁺, $[CH_3COCOO]^-$, and OH⁻.

The degree of chaos of $C_3H_3O_3K(s)$ is increased when it is dissociated to K^+ (aq) and $[CH_3COCOO]^-$ (aq) in the double-distilled water. It is concluded that the entropy change of the dissolution reaction is greater than zero according to the statistical explanation of the entropy in statistical thermodynamics. From the values of molar enthalpies of dissolution, we deduce the conclusion that the dissolution of the title compound in the water is a typical endothermic process, and an entropy-driven process instead of enthalpy-driven process. It mainly ascribes to the breaking of ionic bonds and chelate bonds existing in the compound needing to absorb large amount of heat energy.

Relative partial molar enthalpies

The relative partial molar enthalpies of solvent $(\overline{L_1})$ and solute $(\overline{L_2})$ are important thermodynamic functions of the electrolyte solutions. Generally, there are many ways used to determine the relative partial molar enthalpies. In this paper, they are obtained by the apparent relative molar enthalpy (${}^{\Phi}L$) and partial derivative of ${}^{\Phi}L$ against *m*.

The relative partial molar enthalpy of the double-distilled water $(\overline{L_1})$ as the solvent is expressed as: [16]

$$\bar{L}_1 = -M_{\rm H_2O}m^2 (\partial^{\varphi}L/\partial m)_{\rm T,P}$$
(12)

The formula to determine relative partial molar enthalpy of the compound $(\overline{L_2})$ is,

$$\bar{L}_2 = {}^{\Phi}L + m(\partial^{\Phi}L/\partial m)_{\mathrm{T,P}}$$
(13)

The partial derivative of ${}^{\phi}L$ against *m*, $(\partial^{\phi}L/\partial m)_{T,P}$, is obtained under constant pressure and temperature $(C_{MX}^{\Phi_L})$ is not neglected):

$$(\hat{\sigma}^{\Phi} L/\hat{\sigma} m)_{\mathrm{T,P}} = A_{\mathrm{H}}/(2m^{1/2} + 2.4m) - 2\mathrm{RT}^{2}[\beta_{\mathrm{MX}}^{(0)\mathrm{L}} + \beta_{\mathrm{MX}}^{(1)\mathrm{L}}\exp(-2m^{1/2}) + mC_{\mathrm{MX}}^{\Phi\mathrm{L}}]$$
(14)

According to the relationships shown in Eqs. (7), (12), (13), and (14), apparent relative molar enthalpies (${}^{\Phi}L$) and relative partial molar enthalpies of the double-distilled

water $(\overline{L_1})$ as the solvent and the title compound $(\overline{L_2})$ as the solute are obtained. All the results calculated above are listed in Table 4.

Conclusions

- 1. The potassium pyruvate $C_3H_3O_3K(s)$ is synthesized. The crystal structure is determined by X-ray crystallography. The lattice potential energy of the compound and the volume V_- of the anion CH₃COCOO⁻ are estimated.
- 2. The molar enthalpy of dissolution of the compound at infinite dilution is calculated by Pitzer's electrolyte solution theory. The Pitzer's parameters ($\beta_{MX}^{(0)L}$, $\beta_{MX}^{(1)L}$, and $C_{MX}^{\Phi_L}$) are obtained through fitting of the curve of enthalpy of dissolution with molality of the electrolyte according to Pitzer's theory.
- 3. The values of apparent relative molar enthalpies (${}^{\phi}L$) and relative partial molar enthalpies of the solvent ($\overline{L_1}$) and the compound ($\overline{L_2}$) are derived. These results indicate that the endothermic reaction takes place when it is dissolved in the double-distilled water.
- Finally, the molar enthalpy of hydration of CH₃COCOO⁻(g) is calculated as an important chemical thermodynamic quantity.

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