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The solubility measurements of sodium dicarboxylate salts; sodium oxalate, malonate, succinate, glutarate, and adipate in water from $T = (279.15 \text{ to } 358.15)$ K

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ABSTRACT

The solubility measurements of sodium dicarboxylate salts; sodium oxalate, malonate, succinate, glutarate, and adipate in water at temperatures from (278.15 to 358.15 K) were determined. The molar enthalpies of solution at $T = 298.15$ K were derived: $\Delta_{sol}H_m$ ($m = 2.11$ mol · kg^{-1}) = 13.86 kJ · mol^{-1} for sodium oxalate; $\Delta_{sol}H_m$ ($m = 3.99$ mol · kg^{-1}) = 14.83 kJ · mol^{-1} for sodium malonate; $\Delta_{sol}H_m$ ($m = 2.45$ mol · kg^{-1}) = 14.83 kJ · mol^{-1} for sodium succinate; $\Delta_{sol}H_m$ ($m = 4.53$ mol · kg^{-1}) = 16.55 kJ · mol^{-1} for sodium glutarate, and $\Delta_{sol}H_m$ ($m = 3.52$ mol · kg^{-1}) = 15.70 kJ · mol^{-1} for sodium adipate. The solubility value exhibits a prominent odd–even effect with respect to terms with odd number of sodium dicarboxylate carbon numbers showing much higher solubility. This odd–even effect may have implications for the relative abundance of these compounds in industrial applications and also in the atmospheric aerosols.

1. Introduction

Solubility is a quantitative means of describing the composition of solutions. Solutions may be formed by mixing various combinations of liquids, gases, and solids. Thus, solubility as used to describe a solid dissolved in a liquid would refer to the quantitative composition of the solution. As such, the solubility of a solute may be expressed as the number of moles of solid dissolved in a kilogram of water; such that the units are referred as molality, m (mol · kg^{-1}). Although volumetric measurements are popular in the laboratory for ease of preparation (*i.e.* molar units, or moles of solute per dm^3 of solution), they are inconvenient in terms of physical representations. The concentration changes with temperature and at high concentrations the solute solvent ratio is not proportional to the expressed concentration.

Solubility of sodium succinate and other sodium dicarboxylic salts in water are expressed over the studied temperature range up to 358.15 K. The solubility has been determined on the composition of solid phases in equilibrium with the saturated solutions. Solid dicarboxylates were detected in the observations of the dicarboxylic acids in motor exhaust that prompted speculation the compound may be formed during the direct emissions from combustion sources [1]. They also received much attention because of their roles in forming the heterogenous dicarboxylate-ligand complexation [2] and may contribute to the acidy of precipitation [3]. It is possible that metal–organic complexation enhances the uptake of organic compounds and the solubility of metals in aerosols and also atmospheric water [2]. As an initial step towards a better understanding on the physical chemistry of these compounds, a detailed laboratory study into the solubility of a single acid and salt derivatives has been carried out. It is also particularly noticeable that there is an odd and even effect on the sodium dicarboxylate solubility which may have an influence on the phase and chemical properties of atmospheric aerosols and also have industrial applications.

2. Experimental

2.1. Reagents

The reagents were used throughout this work stated by the molar mass, M_w were: sodium oxalate, $M = 134.00$ g · mol^{-1}; sodium malonate, $M = 148.06$ g · mol^{-1}; sodium succinate, $M = 162.05$ g · mol^{-1}; sodium glutarate, $M = 176.01$ g · mol^{-1}; sodium adipate, $M = 190.00$ g · mol^{-1}. We used the analytical grade reagents with

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mass fraction purity >0.99 with the exception of sodium glutarate and adipate with mass fraction purities ~0.98% and >0.97%, respectively. The substances were used without further purification.

2.2. Solubility determination

The simple apparatus used to determine solubility is shown in figure 1. A two-hole rubber stopper fitted snugly into a test tube (25 mm × 150 mm) of borosilicate glass. The thermometer was inserted carefully through one hole of the rubber stopper so that the thermometer tip was near the bottom of the test tube. A glass rod was inserted through other hole, so that the solution could be agitated. The large borosilicate beaker (2 dm^3) contained water and rested on a hot plate. The solid acids and were weighed accurately, placed in the test tube and distilled water (initially about 2.00 cm^3) was dispensed from the burette into the test tube and recorded to 0.01 cm^3.

The solution in the tube was heated (to about $T = 353$ K) and, once the acid dissolved, it was allowed to cool, while being agitated to determine the temperature at which the acid began to crystallize. The temperature was noted and a small amount of water was added from the burette and recorded. The solution was heated again until the acid dissolved and cooled once more to record a new point of crystal formation. This was repeated many times such that the solubility (ever decreasing) at various temperatures could be determined. These that appear as our results tabulated within figures 2 to 6. Solubility is plotted as the logarithm of the solubility in molal units (ln m vs $1/T$) as this is preferable as the slope of the curve is related to the molar enthalpy of dissolution [13].

3. Results and discussion

The solubility of a solid in a liquid as function of temperature T can be expressed at constant pressure, by the relation:

$$\{\delta \ln m/\delta(1/T)\}(1 + \delta \ln \gamma/\delta \ln m) = -\Delta_{sol}H_m/R, \tag{1}$$

where $\Delta_{sol}H_m$ is the molar enthalpy of solution, R is the gas constant and m and γ are the molality of the solute and its activity coefficient, respectively.

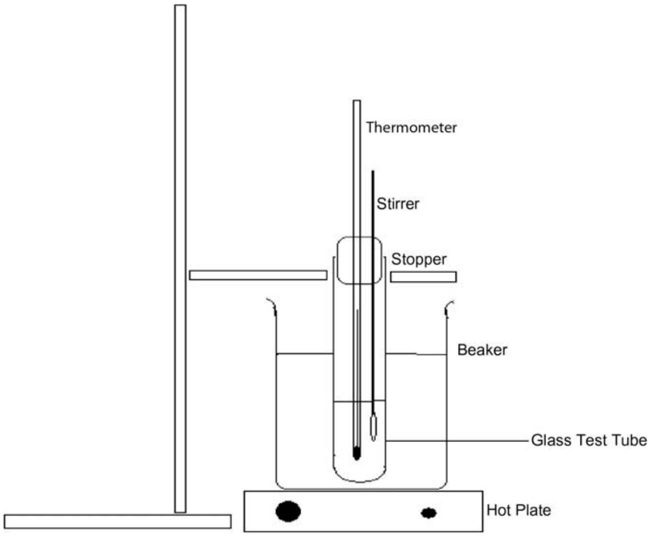

FIGURE 1. The apparatus used to determine solubility.

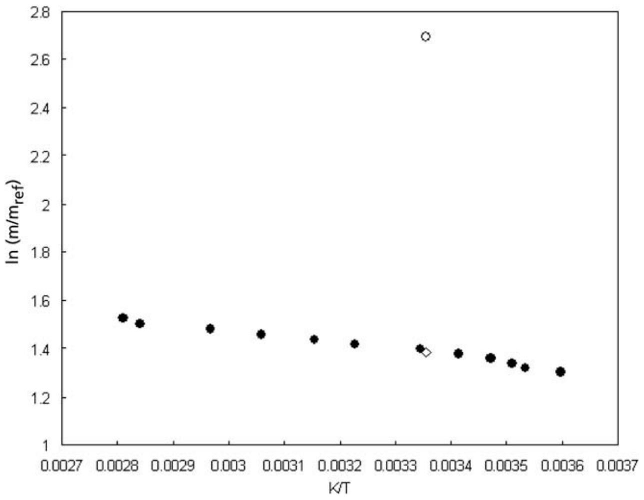

FIGURE 3. Plot of solubility against reciprocal temperature for sodium malonate. This study (black circle), McPherson [9] (open circle); and Tromans [7] (diamond); $m = \text{mol} \cdot \text{kg}^{-1}$, $m_{\text{ref}} = 1.0\ \text{mol} \cdot \text{kg}^{-1}$.

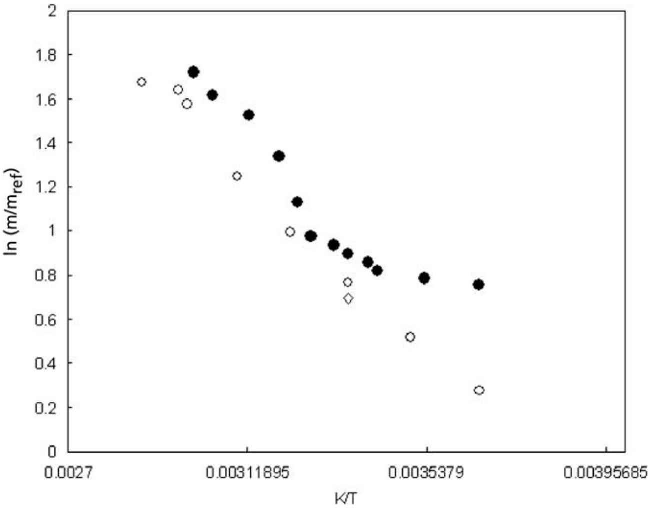

FIGURE 2. Plot of solubility against reciprocal temperature for sodium succinate. Key: this study (black circle); Marshall and Bain [6] (open circle); and Tromans [7] (diamond); $m = \text{mol} \cdot \text{kg}^{-1}$, $m_{\text{ref}} = 1.0\ \text{mol} \cdot \text{kg}^{-1}$.

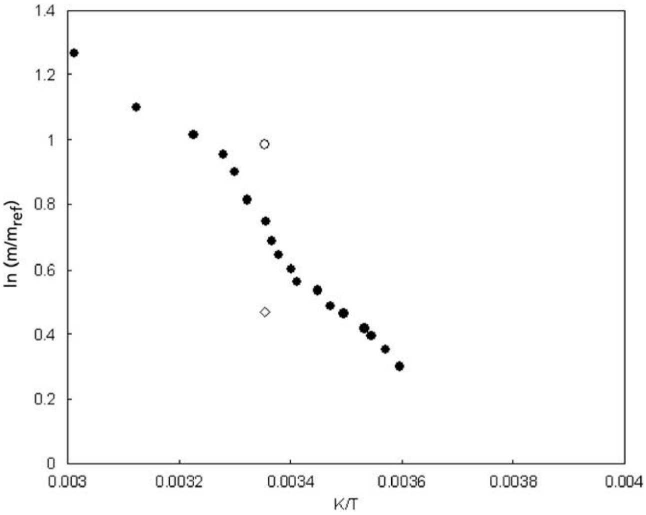

FIGURE 4. Plot of solubility against reciprocal temperature for sodium oxalate. This study (black circle); Broul [10] (open circle); and Tromans [7] (diamond); $m = \text{mol} \cdot \text{kg}^{-1}$, $m_{\text{ref}} = 1.0\ \text{mol} \cdot \text{kg}^{-1}$.

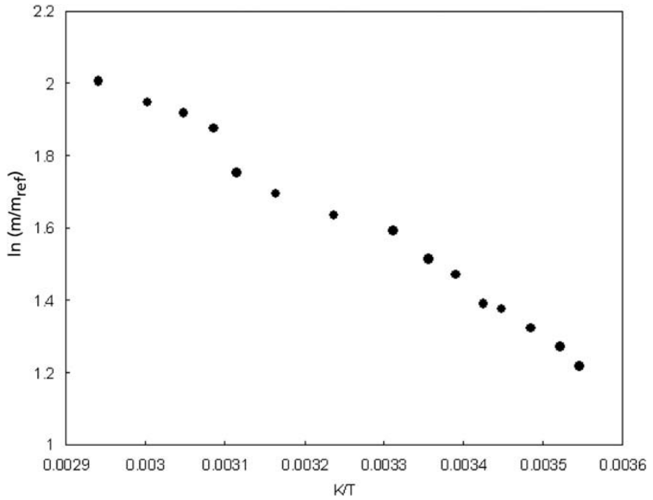

FIGURE 5. Plot of solubility against reciprocal temperature for sodium glutarate. This study (black circle); $m = \text{mol} \cdot \text{kg}^{-1}$, $m_{\text{ref}} = 1.0\ \text{mol} \cdot \text{kg}^{-1}$.

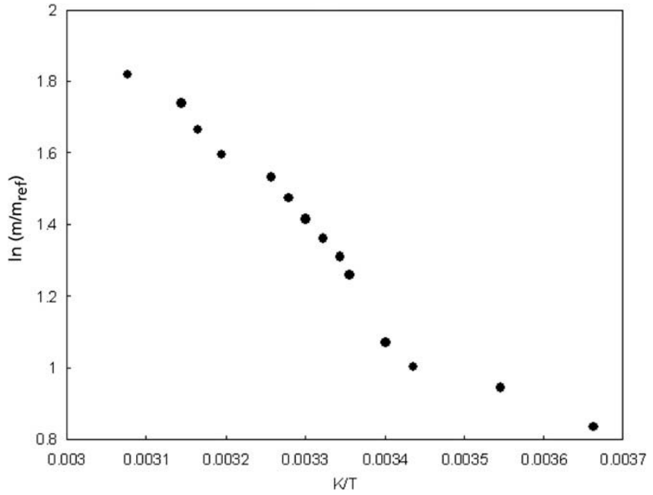

FIGURE 6. Plot of solubility against reciprocal temperature for sodium adipate. Key: this study (black circle); $m = \text{mol} \cdot \text{kg}^{-1}$, $m_{\text{ref}} = 1.0\ \text{mol} \cdot \text{kg}^{-1}$.

At $T = 298.15$ K the solubility of sodium succinate determined from this study is $m = 2.45\ \text{mol} \cdot \text{kg}^{-1}$ (see figure 2) and the same value was established by Linke [4] . This value is slightly higher than those of Marshall and Bain [6] and also by Tromans [7] with $2.05\ \text{mol} \cdot \text{kg}^{-1}$ and $1.92\ \text{mol} \cdot \text{kg}^{-1}$, respectively. Peng *et al.* also carried out the observation of the sodium succinate but rather superficially where he used the electrodynamic balance (EDB) to measure the water activity of selected water soluble organic carbon (WSOC) including sodium malonate and oxalate [5]. From the bulk measurement, he also reported that sodium succinate has the crystallization relative humidity and deliquescent relative humidity of 46.7 to 47.9 and (63.5 to 66) percent, respectively [5]. Since the relative humidity (RH) or water activity (a_w) represents a change in discrete steps in the bulk measurements via EDB, it is difficult to compare the exact value of the saturation condition. The molar enthalpies of solution at $T = 298.15$ K are $\Delta_{sol}H_m$ ($m = 2.45\ \text{mol} \cdot \text{kg}^{-1}$) = $14.83\ \text{kJ} \cdot \text{mol}^{-1}$ and $\Delta_{sol}H_m$ = $15.70\ \text{kJ} \cdot \text{mol}^{-1}$ [6].

The solubility of sodium malonate in figure 3 does not appear to have been measured via saturation determination. However, densities and heat capacities of aqueous sodium malonate have been determined by Tromans with a value of $4\ \text{mol} \cdot \text{kg}^{-1}$ at $T = 298.15$ K [7]. He [7] was unable to prepare $5\ \text{mol} \cdot \text{kg}^{-1}$ solution, and he suggested that the solubility lies between the values of these two molalities. Solid sodium malonate is available in both anhydrous form and as a monohydrate. Sodium malonate also has a solubility of at least $1\ \text{mol} \cdot \text{kg}^{-1}$ at $T = 273.15$ K, since density, viscosity and freezing point depression of aqueous solutions of the salt have been measured at this temperature [8]. McPherson [9] states that solutions of sodium malonate at neutral pH have solubility of about 4 M (this appears to be a molarity, not molality), though it is unclear whether this is at temperature of 300 K where his experiments were carried out [9]. It is worth noting that the neutral pH mentioned would require the addition of some acid to the solution, as calculations suggest that a solution of pure aqueous sodium malonate would have a pH of about 9.5 due to the formation of hydrogen malonate ion in solution. The solubility shown in table 2 of McPherson appears to be a typographical error, or may be the solubility of malonic acid. From this study, the solubility of sodium malonate at $T = 298.15$ K is $3.99\ \text{mol} \cdot \text{kg}^{-1}$ which is similar to the observation by Tromans [7]. The molar enthalpy of the solution is $\Delta_{sol}H_m = 2.18\ \text{kJ} \cdot \text{mol}^{-1}$.

At $T = 298$ K, the solubility of sodium oxalate from our study is $2.11\ \text{mol} \cdot \text{kg}^{-1}$ while that by Tromans is $1.78\ \text{mol} \cdot \text{kg}^{-1}$ (figure 4). Broul *et al.* [10] reported that at the same temperature sodium oxalate is rather more soluble with a value of $2.68\ \text{mol} \cdot \text{kg}^{-1}$. Peng *et al.* also reported that the bulk data measured in his study do not overlap with the single particle results and therefore he assumed that the anhydrous state at relative humidity 0% was used as the reference state for calculating the mass fraction of solute (mfs) [5]. This assumption appears to be valid since the supersaturated data follow a consistent trend with the bulk data and indeed, sodium oxalate crystallizes to form an anhydrous salt which only in the solid state at $T = 298$ K as reported by Linke [4].

The solubility of sodium oxalate and the molar enthalpy values of the solution at $T = 298.15$ K is $\Delta_{sol}H_m$ ($m = 2.11\ \text{mol} \cdot \text{kg}^{-1}$) = $13.86\ \text{kJ} \cdot \text{mol}^{-1}$. Tromans [7] explained that using the calorimeter asymmetry frequently results in a small discrepancy, a point noticed by several authors. However, it is a perfect method to determine the molar enthalpy of substances.

There is no literature available for sodium glutarate (figure 5) and sodium adipate (figure 6) in water. Indeed, the solubility determinations of both solid dicarboxylates were carried out using approximately the same procedure as used for sodium succinate. At $T = 298.15$ K, the solubility of each compound is $m = 4.532\ \text{mol} \cdot \text{kg}^{-1}$ and $m = 3.52\ \text{mol} \cdot \text{kg}^{-1}$, respectively and the molar enthalpy

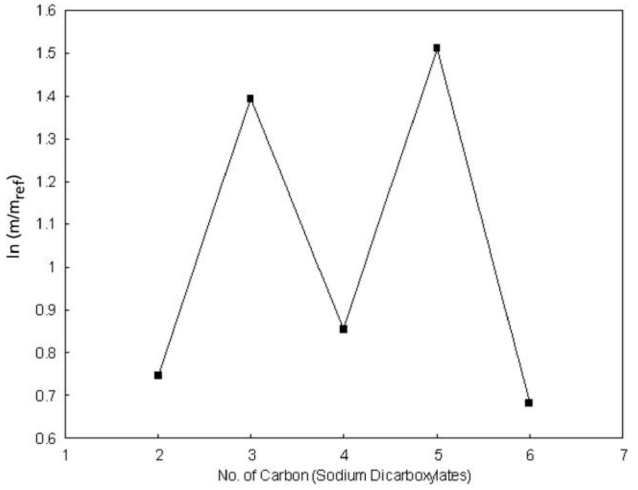

FIGURE 7. Plot of solubility against number of carbon atoms in the chain of the sodium dicarboxylates in the water at $T = 298.15$ K, $m_{\text{ref}} = 1.0\ \text{mol} \cdot \text{kg}^{-1}$.

of each solution is $\Delta_{sol}H_m = 10.55\ \text{kJ} \cdot \text{mol}^{-1}$ for sodium glutarate and $\Delta_{sol}H_m = 15.70\ \text{kJ} \cdot \text{mol}^{-1}$ for sodium adipate.

The series of dicarboxylate compounds also showed the affect of the odd–even numbers of carbon atoms on physical properties. The aqueous solubility in acid of the sodium dicarboxylate salt is highly dependent on the number of carbon atoms with odd numbers of carbon atoms being much more soluble than those with even numbers.

Sodium oxalate, adipate and succinate (even carbon numbers) have much lower solubility than the sodium malonate and glutarate which are exceptionally soluble. Published values of solubility of the dicarboxylic acids are presented as function of the number of carbons in sodium dicarboxylate compounds in figure 7. A number of previous authors have observed this noticeable odd–even effect with dicarboxylic acid solubility [11–13].

4. Conclusion

The presence of the sodium dicarboxylate compound in the solutions containing dissolved aqueous electrolyte have an influence in the multiphase aerosol solubility and also in the industrial applications. This is an important consideration in aqueous systems which are likely to be complex and contain salts as well as both electrolyte and organic compound in solution. One valuable finding also has been discovered from the observation that the solubility of sodium dicarboxylate compounds in aqueous solution shows and odd and even pattern. Compound with odd numbers of acid carbon (sodium malonate and glutarate) have much higher solubility than the even (sodium succinate, oxalate, and adipate). Although odd–even effects have been observed before, they are typically quite small (a few percent difference in vapour pressure, etc.), the effect on the solubility of sodium dicarboxylate shows a magnitude differences.

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JCT 07-198