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Determination and modeling of aqueous solubility of 4-position substituted benzoic acid compounds in a high-temperature solution

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ABSTRACT

Accurate experimental determination of the aqueous solubility of 4-position substituted benzoic acid compounds in a high-temperature solution and its correlation are presented. The temperature effect dependence of aqueous solubility was investigated in the range from 303.15 to 473.15 K. The solubility prediction is essential for rapid design and optimization of separation, purification and formulation processes in the chemical industry. Solubility data were determined using a simple and reliable apparatus and analyzed by the classical titration method. Experimental data were regressed with the modified Apelblat equation and the λH equation. The λH equation gave good agreement with all experimental data. A solubility model modified from the λH equation was used to correlate the experimental data. The percentage of average relative deviations of these correlations was 1.40% for the solubility of 4-acetylbenzoic acid in an aqueous solution.

1. Introduction

Solubility is one of the most fundamental physicochemical properties. It is particularly useful for a wide variety of applications important in the biological, chemical and environmental industries [1]. Accurate solubility data are needed for process and product design, including production and purification of chemical compounds [2], separation [3], precipitation processes [4], crystallization processes [5], chemical reaction systems [6], pollution prevention [7], and biomass processing [8]. There are a vast amount of papers in the available literature reporting the results of solubility measurements in aqueous solutions [9–12].

The 4-position substituted benzoic acid compounds which are considered as important priority contaminants or typical environmental pollutants may have an adverse impact on the environment in a number of ways and represent a great potential risk to human health [13,14]. They are widely used as reaction intermediates [15,16], and are often formed as a result of the degradation of aromatic compounds. In the polyester industry, a large amount of residue is formed during the manufacturing process of purified terephthalic acid (Fig. 1a) [17,18]. The 4-position substituted benzoic acid compounds–such as 4-formylbenzoic acid (Fig. 1b), 4-acetylbenzoic acid (Fig. 1c), 4-methylbenzoic acid (Fig. 1d) and 4-*tert*-butylbenzoic acid (Fig. 1e)–should be the components in this residue [19]. For the sake of environmental protection and sufficient utilization of natural resources, it is necessary to pay attention to the separation and recovery of oxidation residues [20–22]. To recover useful components from these residues, comprehensive solubility data are required. From the literature it is known that some compounds have a very low solubility while others can only exist in a liquid phase state over a narrow temperature range [23–25]. Therefore, they are not particularly suitable for a recovery process. Thus, systematic and comprehensive measurement of solubility data of 4-position substituted benzoic acid compounds in aqueous solutions over a wide temperature range is needed.

In this work, the solubility of 4-position substituted benzoic acid compounds in an aqueous solution was measured as a function of temperature over a temperature range from 303.15 to 473.15 K. The solubility of 4-position substituted benzoic acid compounds in an aqueous solution was well described by an empirical formula [26]. The capability of selected equilibrium models of experimental data was described. The modified Apelblat equation [27–29] and the λH equation [30,31] were used to correlate the experimental data, and parameters of the models were obtained. It is found that the modified Apelblat equation model gives good agreement with all experimental data. The above-mentioned models are rapid and easy methods which provide acceptable values of solubility as a function of temperature.

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Nomenclature

A,B,C	constant parameters in the correlated modified Apelblat model
A.D.	absolute relative deviation (%)
A.A.D.	average absolute relative deviation (%)
D	density of solvent (g/mL)
$\Delta_m H^f_a$	molar enthalpy of fusion (kJ/mol^{-1})
H	constant parameters in the correlated λ*H* model
K_1	constant parameters in the empirical formula model
K_2	constant parameters in the empirical formula model
T	experimental temperature (K)
T_m	melting temperature (K)
R^2	squared regression coefficients
x	mole fraction

Greek letters

λ	constant parameters in the correlated λ*H* model

Subscripts

i	each 4-position substituted benzoic acid compound
c	calculated result
e	experimental data
mA.c.	modified Apelblat model calculated result
H.c.	λ*H* model calculated result
S	solvent

2. Experimental

2.1. Materials

Terephthalic acid ($C_8H_6O_4$, molecular weight 166.13 g/mol), 4-formylbenzoic acid ($C_8H_6O_3$, molecular weight 150.13 g/mol), 4-acetylbenzoic acid ($C_9H_8O_3$, molecular weight 164.16 g/mol), 4-methylbenzoic acid ($C_8H_8O_2$, molecular weight 136.15 g/mol) 4-*tert*-butylbenzoic acid ($C_{11}H_{14}O_2$, molecular weight 178.23 g/mol) and benzoic acid ($C_7H_6O_2$, molecular weight 122.12 g/mol) were obtained from Sigma-Aldrich. The reagents and solvents used in the experiments were of GR grade and were purchased from Mikrochem®, Pezinok, Slovakia. The melting temperatures (T_m) and the enthalpies of fusion ($\Delta_m H^f_a$) of the benzoic acid derivatives [32,33] are listed in Table 1. These compounds were used without further purification. Aqueous solutions of 4-position substituted benzoic acid were prepared using redistilled water.

Table 1
Melting temperatures and enthalpies of fusion of the 4-position substituted benzoic acid compounds.

Compounds	T_m/K	$\Delta_m H^f_a$ (kJ mol^{-1})
Benzoic acid	396.15	17.9883
4-*tert*-butylbenzoic acid	438.15	17.8943
4-methylbenzoic acid	453.15	22.5878
4-formylbenzoic acid	523.15	25.7490
4-acetylbenzoic acid	483.15	20.7039
Terephthalic acid	573.15	63.4284

2.2. Apparatus and procedure

The solubility of 4-position substituted benzoic acid compounds in an aqueous solution was measured by the equilibrium method, which is a frequently used for determination of solubility. The experimental apparatus (Fig. 2) consisted of a 50 mL stainless steel closed vessel equipped with a magnetic stirrer; 25 mL of redistilled water was used to dissolve the acids which were weighed with an accuracy of 0.0001 g. After the solid-liquid system was sufficiently mixed, the experimental run could be performed. The vessel was heated in a thermostated silicone oil bath with an accuracy of ± 0.1 K.

The preliminary experiments showed that, after 90 min of stirring, equilibrium was achieved and the concentration of 4-position substituted benzoic acid compounds in the liquid solution became constant. Then, the system was put into a static state for 120 min. During this time the solution became homogeneous, and all suspended particles were deposited on the bottom. Then, at the experimental temperature, a Teflon® container was pushed into the solution, and by switching to the sampling position a sample of the solution (about 0.5 mL) was withdrawn. To avoid the loss of solvents by vaporization during sampling, the valve of the Teflon® container was quickly closed and the vessel cooled to ambient temperature with cooling water. After opening the vessel, the closed Teflon® container was washed three times with 100 mL distilled water and then air-dried. The amount of the sample withdrawn into the Teflon® container was determined as the difference between the weight of the container before and after sampling.

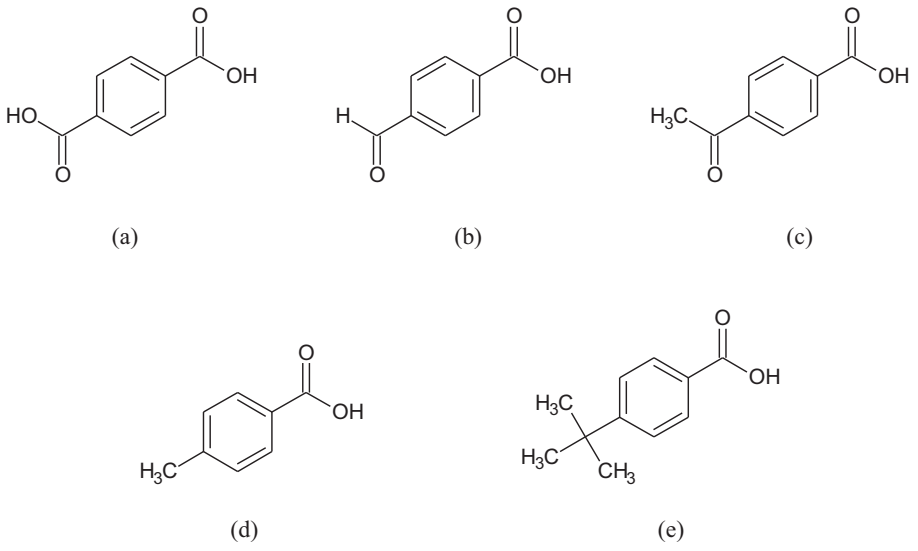

Fig. 1. The structures of (a) terephthalic acid, (b) 4-formylbenzoic acid, (c) 4-acetylbenzoic acid, (d) 4-methylbenzoic acid, (e) 4-*tert*-butylbenzoic acid.