

APPENDICES

APPENDIX A

APPENDIX A

DETERMINATION AND MODELING OF AQUEOUS SOLUBILITY OF
4-POSITION SUBSTITUENTED BENZOIC ACID COMPOUNDS
IN A HIGH-TEMPERATURE SOLUTION

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A.1 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 modified Apelblat equation gave good agreement with all experimental data. A solubility model modified from a modified Apelblat model 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.

A.2 INTRODUCTION

Solubility is one of the most fundamental physico-chemical 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 (Figure A.1(a)) [17, 18]. The 4-position substituted benzoic acid compounds – such as 4-formylbenzoic acid

(Figure A.1(b)), 4-acetylbenzoic acid (Figure A.1(c)), 4-methylbenzoic acid (Figure A.1(d)) and 4-*tert*-butylbenzoic acid (Figure A.1(e)) – 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 was 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.

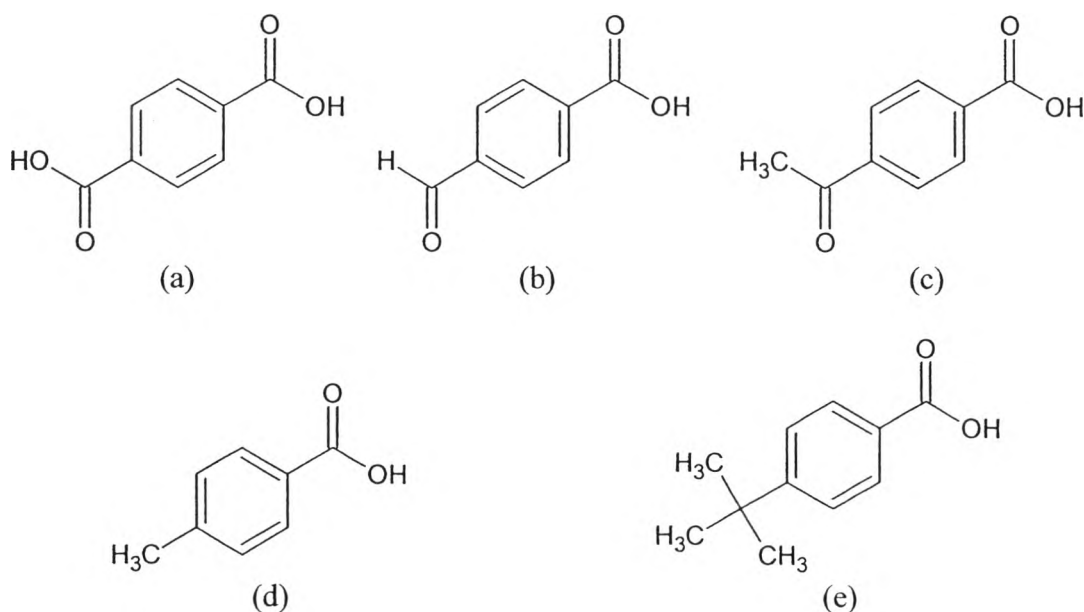


Figure A.1 The structures of (a) terephthalic acid, (b) 4-formylbenzoic acid, (c) 4-acetylbenzoic acid, (d) 4-methylbenzoic acid, (e) 4-*tert*-butylbenzoic acid

A.3 EXPERIMENT

A.3.1 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 ($\Delta_m H_a^f$) of the benzoic acid derivatives [32, 33] are listed in Table A.1. These compounds were used without further purification. Aqueous solutions of 4-position substituted benzoic acid were prepared using redistilled water.

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

Compounds	T_m/K	$\Delta_m H_a^f$ (kJ mol ⁻¹)
Benzoic acid	396.15	17.9883
4- <i>tert</i> -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

A.3.2 Apparatus and procedures

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 (Figure A.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. After opening the container, the withdrawn sample was transferred into a volumetric flask and then analyzed by titration method. For titration, aqueous solutions of sodium hydroxide and hydrochloric acid with phenolphthalein as an indicator were used. Each experiment was repeated at least twice. The conversion between molarity and mole-fraction concentration scales used the density of the saturated solutions, which was determined with a digital density meter (LiquiPhysics[™] Excellence; Mettler-Toledo, Greifensee, Switzerland).

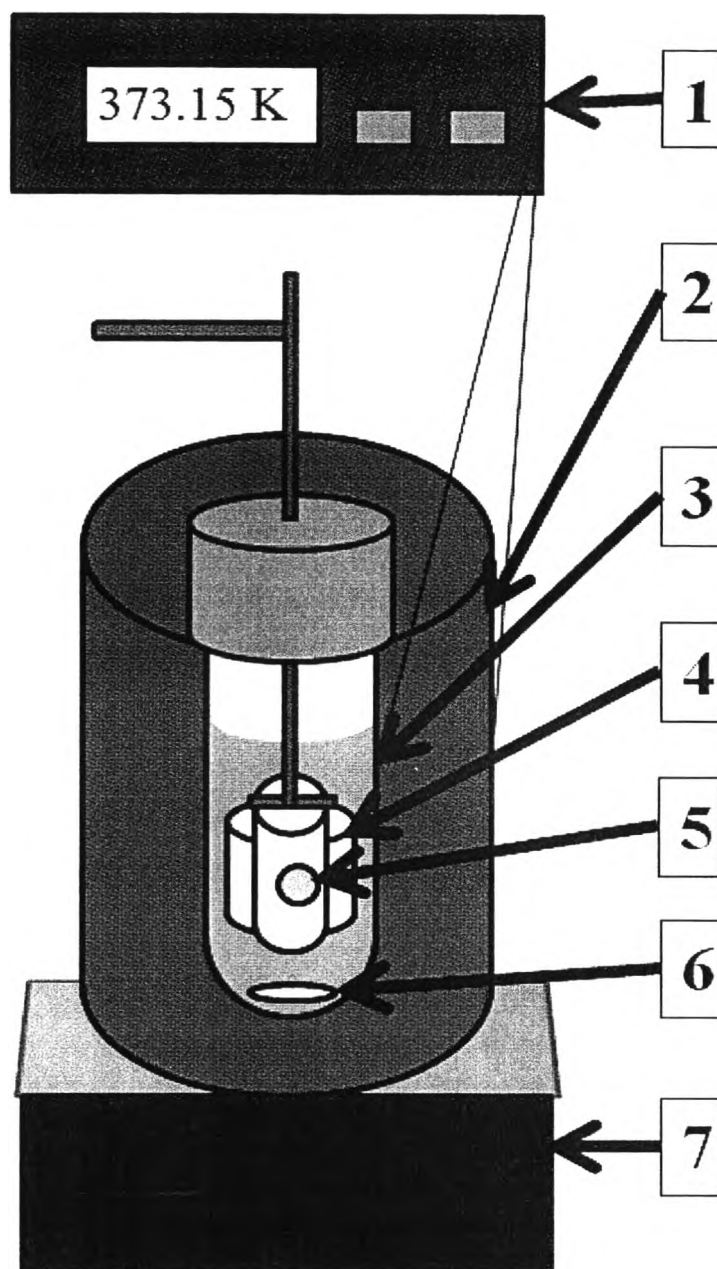


Figure A.2 The experimental apparatus

1. Temperature control 2. Silicone oil bath 3. Stainless steel vessel 4. Teflon[®] container 5. Sampling vessel 6. Magnetic stirrer 7. Stirrer controller

A.4 RESULTS AND DISCUSSION

A.4.1 Experimental results

In this study the solubility measurement technique was validated by comparing with solubility data in the literature [24, 25, 34–36]. The solubility data of the 4-position substituted benzoic acid compounds in an aqueous solution are shown in Table A.2, in which T is the absolute temperature and x_e is the experimentally measured mole fraction. Only a few reports have published data concerning the solubility of 4-position substituted benzoic acid compounds in aqueous solutions at higher temperatures [24–26]. Figures A.3 and A.4 show that our experimental data are in good agreement with the literature [24, 25, 35, 36].

The experiments reveal that the solubility of the above-mentioned compounds increases with temperature. In Figures A.3 and A.4 the solubility measurements obtained by different researchers are compared. Solubility data for benzoic acid derivatives are also available in the literature [26, 37, 38], but only for narrow and low temperature ranges. The solubility data of terephthalic acid, 4-formylbenzoic acid, 4-methylbenzoic acid and benzoic acid in water as a function of temperature (T) or for a few temperatures were determined by Wang et al. [24], Sun et al. [36], Li et al. [39] and Strong [40]. The temperature dependence of the solubility of 4-acetylbenzoic acid and 4-tert-butylbenzoic acid in aqueous solutions has not been investigated previously. Our results are shown in Table A.2. The solubility data presented here and the measurements published in the literature are in a good agreement, particularly for benzoic acid, 4-formylbenzoic acid and 4-methylbenzoic acid. The differences between our work and the works of Strong [40], Sun et al. [36] and Li et al. [39] can be attributed to some extent by different experimental approaches. In the case of low solubility (in particular, the extremely low solubility of 4-position substituted benzoic acid compounds), analysis and especially the separation of solids dispersed in the liquid phase are difficult and sensitive to deviations. As a consequence, slight deviations between different solubility experiments can be considered acceptable.

Table A.2 The aqueous solubility data of 4-position substituted benzoic acid compounds at high temperatures

(a) The aqueous solubility data of benzoic acid

T/K	$10^3 x_e$	$10^3 x_{mAc}$	$A.D._{mAc}(\%)$	$10^3 x_{lHc}$	$A.D._{lHc}(\%)$
423.15	40.30	40.38	0.20	40.34	0.10
413.15	29.60	29.84	0.81	29.81	0.71
403.15	21.21	21.85	3.04	21.52	1.48
393.15	15.50	15.90	2.58	15.70	1.29
383.15	10.45	10.49	0.39	10.52	0.68
373.15	9.13	9.24	1.21	9.21	0.88
363.15	6.30	5.85	7.14	6.18	1.90
353.15	4.19	4.13	1.52	4.12	1.76
343.15	2.68	2.69	0.52	2.70	0.89
333.15	1.81	1.90	5.25	1.85	2.48
323.15	1.43	1.36	4.63	1.39	2.53
313.15	0.89	0.92	3.37	0.90	1.12
303.15	0.62	0.62	0.00	0.62	0.00
<i>A.A.D. (%)</i>			<u>2.36</u>		<u>1.22</u>

(b) The aqueous solubility data of 4-*tert*-butylbenzoic acid

T/K	$10^3 x_e$	$10^3 x_{mAc}$	$A.D._{mAc}(\%)$	$10^3 x_{lHc}$	$A.D._{lHc}(\%)$
423.15	40.39	40.10	0.72	40.51	0.30
413.15	29.68	29.60	0.27	29.66	0.07
403.15	21.20	21.67	2.22	21.60	1.89
393.15	15.50	15.73	1.48	15.22	1.81
383.15	10.45	11.31	8.20	10.73	2.68
373.15	9.12	8.04	11.84	9.11	0.11
363.15	5.56	5.66	1.80	5.62	1.08
353.15	3.89	3.94	1.29	3.75	3.60
343.15	2.50	2.71	8.40	2.64	5.60
333.15	1.63	1.84	12.88	1.60	1.84
323.15	1.53	1.23	19.61	1.51	1.31
313.15	0.80	0.81	1.25	0.82	2.50
303.15	0.50	0.52	4.00	0.50	0.00
<i>A.A.D. (%)</i>			<u>5.69</u>		<u>1.75</u>

(c) The aqueous solubility data of 4-methylbenzoic acid

T/K	$10^3 x_e$	$10^3 x_{mA.c.}$	$A.D._{mA.c.}(\%)$	$10^3 x_{\lambda H.c.}$	$A.D._{\lambda H.c.}(\%)$
443.15	48.93	51.94	6.15	48.04	1.82
433.15	39.82	40.96	2.86	39.11	1.78
423.15	13.48	13.58	0.74	13.98	3.71
413.15	11.23	11.05	1.60	11.09	1.25
403.15	7.14	6.63	7.14	7.54	5.60
393.15	4.55	3.99	12.31	4.69	3.08
383.15	2.77	2.41	13.00	2.89	4.33
373.15	1.83	1.46	20.22	1.81	1.09
363.15	0.71	0.79	11.27	0.73	2.82
353.15	0.51	0.55	7.84	0.52	1.96
343.15	0.36	0.34	5.56	0.35	2.78
333.15	0.19	0.22	15.79	0.20	5.26
323.15	0.14	0.14	0.00	0.15	7.14
313.15	0.10	0.09	10.00	0.11	10.00
303.15	0.06	0.07	16.67	0.06	0.00
298.15	0.05	0.05	0.00	0.05	0.00
<i>A.A.D. (%)</i>			<u>8.20</u>		<u>3.29</u>

(d) The aqueous solubility data of 4-formylbenzoic acid

T/K	$10^3 x_e$	$10^3 x_{mAc}$	$A.D._{mAc}(\%)$	$10^3 x_{lHc}$	$A.D._{lHc}(\%)$
473.15	3.35	3.41	1.79	3.38	0.90
463.15	2.86	2.90	1.40	2.80	2.10
453.15	2.42	2.21	8.68	2.38	1.65
443.15	2.03	2.05	0.99	1.99	1.97
433.15	1.69	1.71	1.18	1.64	2.96
423.15	1.47	1.53	4.08	1.49	1.36
413.15	1.20	1.11	7.50	1.19	0.83
403.15	1.02	1.09	6.86	0.98	3.92
393.15	0.67	0.66	1.49	0.66	1.49
383.15	0.52	0.49	5.77	0.49	5.77
373.15	0.46	0.42	8.70	0.42	9.78
363.15	0.36	0.37	2.78	0.37	2.78
353.15	0.33	0.32	3.03	0.32	3.03
343.15	0.25	0.26	4.00	0.24	4.00
333.15	0.23	0.24	4.35	0.23	0.00
323.15	0.17	0.19	11.76	0.18	5.88
313.15	0.11	0.10	9.09	0.12	9.09
303.15	0.08	0.08	0.00	0.08	0.00
$A.A.D.(\%)$			<u>4.64</u>		<u>3.20</u>

(e) The aqueous solubility data of 4-acetylbenzoic acid

T/K	$10^3 x_e$	$10^3 x_{mAc}$	$A.D._{mAc}(\%)$	$10^3 x_{lHc}$	$A.D._{lHc}(\%)$
473.15	10.40	10.72	3.08	10.36	0.38
463.15	8.31	8.38	0.84	8.21	1.20
453.15	6.30	6.54	3.81	6.31	0.16
443.15	4.59	5.09	10.89	4.68	1.96
433.15	4.05	3.95	2.47	3.92	3.21
423.15	3.08	3.06	0.65	3.07	0.32
413.15	2.38	2.36	0.84	2.38	0.00
403.15	1.78	1.82	2.25	1.83	2.81
393.15	1.36	1.40	2.94	1.40	2.94
383.15	1.04	1.07	2.88	1.05	0.96
373.15	0.80	0.82	2.50	0.79	1.25
363.15	0.61	0.63	3.28	0.61	0.00
353.15	0.46	0.48	4.35	0.47	2.17
343.15	0.35	0.36	2.86	0.36	2.86
333.15	0.27	0.28	3.70	0.27	0.00
323.15	0.20	0.21	5.00	0.21	5.00
313.15	0.16	0.16	0.00	0.16	0.00
303.15	0.12	0.12	0.00	0.12	0.00
<i>A.A.D. (%)</i>			<u>2.91</u>		<u>1.40</u>

(f) The aqueous solubility data of terephthalic acid

T/K	$10^5 x_e$	$10^5 x_{mA.c.}$	$A.D._{mA.c.}(\%)$	$10^5 x_{\lambda H.c.}$	$A.D._{\lambda H.c.}(\%)$
473.15	1.63	1.72	5.52	1.68	3.07
463.15	1.28	1.30	1.56	1.29	0.78
453.15	0.94	0.98	4.26	0.96	2.13
443.15	0.79	0.74	6.33	0.76	3.80
433.15	0.69	0.56	18.84	0.62	10.14
423.15	0.39	0.42	7.69	0.40	2.56
413.15	0.32	0.32	0.00	0.32	0.00
403.15	0.26	0.24	7.69	0.25	3.85
393.15	0.19	0.18	5.26	0.19	0.00
383.15	0.13	0.14	7.69	0.13	0.00
373.15	0.08	0.09	12.50	0.09	12.50
363.15	0.07	0.08	14.29	0.08	14.29
353.15	0.06	0.06	0.00	0.06	0.00
343.15	0.05	0.05	0.00	0.05	0.00
333.15	0.04	0.04	0.00	0.04	0.00
323.15	0.03	0.03	0.00	0.03	0.00
313.15	0.02	0.02	0.00	0.02	0.00
303.15	0.02	0.02	0.00	0.02	0.00
<i>A.A.D.</i> (%)			<u>5.09</u>		<u>2.95</u>

A.4.2 Effect of 4-position substituted groups on solubility

A.4.2.1 Inductive effect of electron-donating groups on the solubility of 4-position substituted benzoic acid compounds

The inductive effect of electron-donating groups on the solubility of substituted benzoic acid compounds is especially valid when the substituent is attached to the 2-position or 4-position. The inductive effect is usually the main effect. This effect is shown below for a series of 4-position substituted benzoic acids groups. The alkyl-substituted groups such as methyl and *tert*-butyl are electron-donating groups. The electron-donating substituents have a positive inductive effect. The alkyl-substituted group on the benzoic acid will donate electrons to the carboxylic group. The negative charge of the alkyl-substituted group is destabilizing to the carboxylate ion. Therefore, the solubility of 4-methylbenzoic acid is generally lower than that of benzoic acid. These results are shown in Figure A.3.

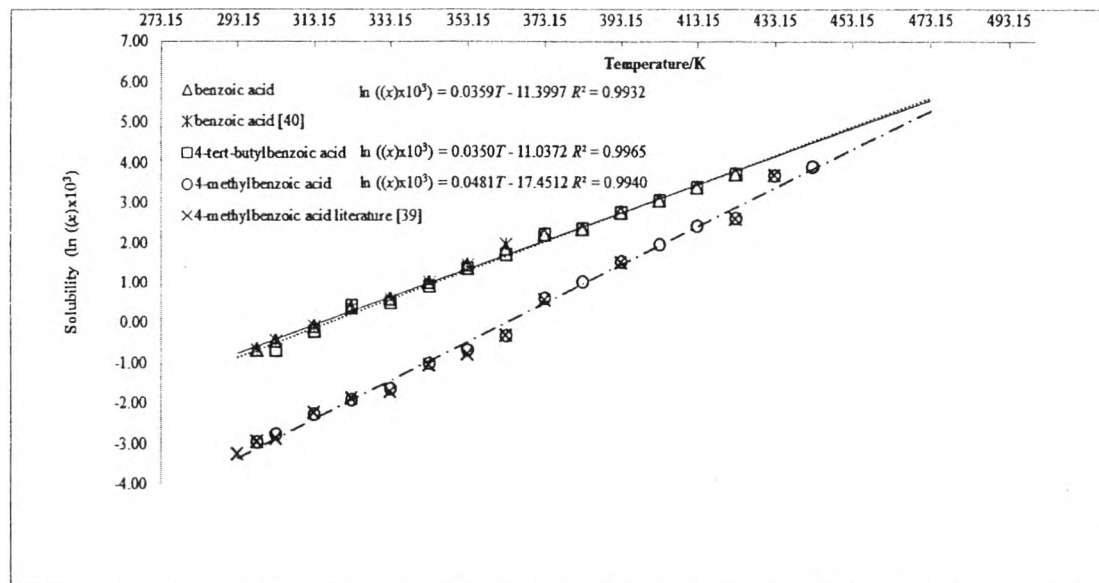


Figure A.3 The solubility data and empirical formula model correlation of 4-position substituted benzoic acid compounds with electron-donating groups compared with the literature data

A.4.2.2 Inductive and resonance effects of electron-withdrawing groups on the solubility of 4-position substituted benzoic acid compounds

Figure A.4 shows the experimental solubility of 4-position substituted benzoic acid compounds containing electron-withdrawing groups in an aqueous solution. The electronegative groups increase their solubility. Because electronegative groups decrease electron density from the anion (conjugate base), they stabilize the carboxylate ion. The electronegative substituted groups, such as formyl and acetyl groups, are electron-withdrawing groups. The electron-withdrawing groups have inductive and resonance effects. Generally these effects increase the solubility, regardless of the position, because they stabilize the anion (conjugate base) by delocalizing the charge through resonance and inductive effects. The solubility of the 4-position electron-withdrawing substituted benzoic acid compounds increases when the conjugate base of the 4-position substituted benzoic acid compounds is stabilized by resonance. Because resonance leads to charge delocalization, it lowers the energy, which leads to higher stability. Resonance effects are particularly important in substituted aromatic compounds such as benzoic acids and substituted benzoic acids. Resonance affects the ionization values, especially when substituents are located at the 2-position and 4-position. In the case of benzene dicarboxylic acids, two

carboxylic groups are electronegative groups. These groups together decrease the electron density, and the ionization of the molecule is very low. Therefore, the solubility of benzene dicarboxylic acids, such as terephthalic acid, is generally lower than the solubility of benzoic acid.

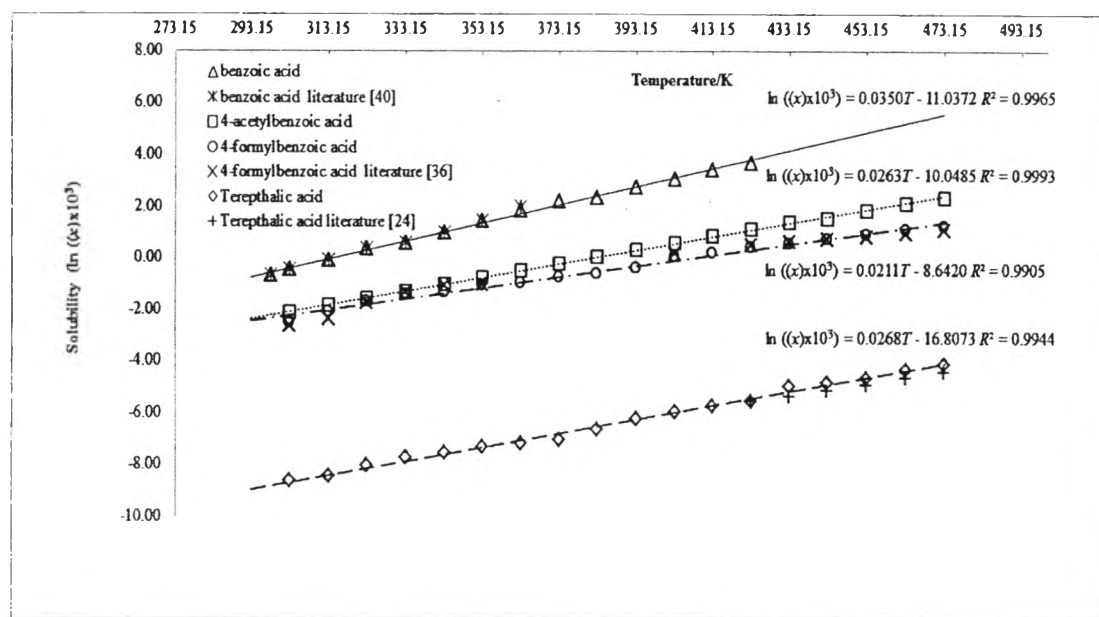


Figure A.4 The solubility data and empirical formula model correlation of 4-position substituted benzoic acid compounds with electron-withdrawing groups compared with the literature data

A.4.3 Models for solubility calculations

For the solid-liquid equilibrium, several models [41] using the activity coefficient can be applied, e.g. the empirical formula model [26], the Wilson equation model, the modified Apelblat equation model, the λH equation model, NRTL, UNIQUAC and UNIFAC. In this study, the empirical formula model, the modified Apelblat equation and the λH equation models were chosen. The modified Apelblat model is a widely used semi-empirical model, suitable for nonpolar and polar systems. The λH equation model has the advantage of having two adjustable parameters, λ and H , which allows its use in fitting the experimental data well for many systems. It is proposed for the direct correlation of solid-liquid equilibrium, and it is widely accepted to be capable of dealing with strong polarity systems [41, 42],

which involve strong interaction between molecules. The results of the correlations using the modified Apelblat equation and λH equation models are discussed below.

A.4.3.1 Empirical formula

In this work, an empirical formula [26] represented by Eq. (A.1) was used to correlate the aqueous solubility of the 4-position substituted benzoic acid compounds, for both the presented results and the results available in the literature [26, 37, 38]. All regressions produced high correlation coefficients. The squared regression coefficients (R^2) for 4-*tert*-butylbenzoic acid and 4-acetylbenzoic acid were higher than 0.99. The results are shown in Figures 4.3 and 4.4 indicate that the equations can satisfactorily describe the experimental data obtained from the models. The empirical formula used in this work can be written as:

$$x = K_1 \exp(K_2 T) \quad (\text{A.1})$$

where T is the absolute temperature, and K_1 and K_2 are two constant parameters for the empirical formula model.

A.4.3.2 The modified Apelblat equation

The modified Apelblat equation gives the following expression obtained from the Clausius–Clapeyron equation [27, 43]. The assumption of the modified Apelblat equation is that the enthalpy of a solution is directly proportional to the temperature [43–45]. The modified Apelblat equation has the following form:

$$\ln x = A + \frac{B}{T} + C \ln(T) \quad (\text{A.2})$$

where T is the absolute temperature, and A , B and C are three parameters obtained by fitting the experimental solubility data.

Eq. (A.2) is used to correlate the solubility of 4-position substituted benzoic acid compounds in an aqueous solution. The parameters A , B and C were estimated by correlating the experimental data, and were evaluated by using a non-linear optimization method [46], in which the objective function was the percentage of

absolute relative deviation (*A.D.* (%)) between the experimental and calculated model mole fraction of 4-position substituted benzoic acid compounds.

The experimental data, the calculated values and the percentage of absolute relative deviation (*A.D.* %) are presented in Table 4.2. The definition of *A.D.* (%) is given by the following relation:

$$A.D.(%) = \frac{|x_e - x_c|}{x_e} \times 100 \quad (A.3)$$

where x_e is the experimentally measured mole fraction of a solute compound in an aqueous solution, and x_c is the value calculated by Eq. (A.2).

The regressed parameter values are listed in Table 4.3. The measured data and modified Apelblat model of the aqueous solubility of 4-position substituted benzoic acid compounds in a high-temperature solution are shown in Figures A.5 and A.6. All squared regression coefficients (R^2) are greater than 0.99. The regression shows that the model is a good fit with the experimental data.

Table A.3 The parameters in the modified Apelblat equation model for different 4-position substituted benzoic acid compounds

Compounds	modified Apelblat equation model			
	A	B	C	R^2
Benzoic acid	-80.57	445.00	13.76	0.9980
4- <i>tert</i> -butylbenzoic acid	-61.03	-712.00	10.98	0.9950
4-methylbenzoic acid	-306.39	10657.00	46.98	0.9950
4-formylbenzoic acid	-49.69	-55.00	8.25	0.9940
4-acetylbenzoic acid	-111.84	2836.10	17.57	1.0000
Terephthalic acid	-167.40	5446.00	24.65	0.9950

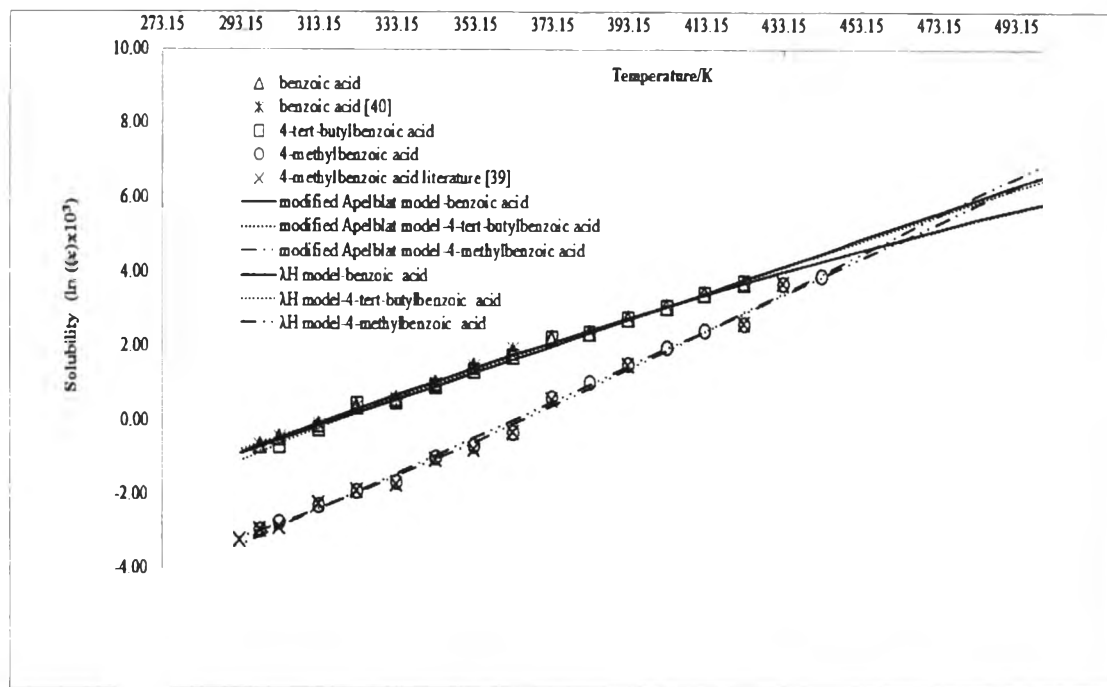


Figure A.5 The solubility data and model correlation of 4-position substituted benzoic acid compounds with electron-donating groups

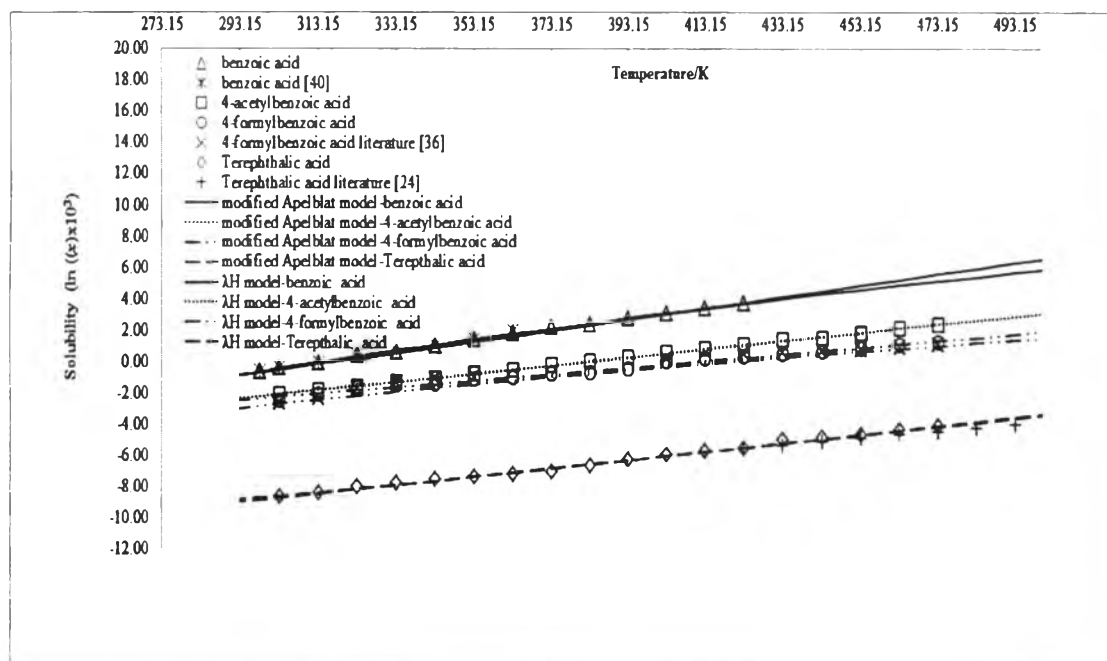


Figure A.6 The solubility data and model correlation of 4-position substituted benzoic acid compounds with electron-withdrawing groups

A.4.3.3 Buchowski–Książczak equation (λH equation)

Buchowski et al. [42] studied the relationships between activity, solubility and temperature. The Buchowski–Książczak equation was also selected to fit the experimental data. It is proposed for the direct correlation of solid-liquid equilibrium; it is also widely accepted as being capable of dealing with strong polarity systems, which involve strong interaction between molecules. It is more commonly known as the λH equation because of the two parameters (λ and H) in the equation, and has the following form:

$$\ln \left[1 + \frac{\lambda(1-x_i)}{x_i} \right] = \lambda H \left[\frac{1}{T} - \frac{1}{T_m} \right] \quad (\text{A.4})$$

where T_m is the normal melting temperature of 4-position substituted benzoic acid compounds, λ and H are the two equation parameters, and x_i represents the mole fraction of a solute compound in an aqueous saturated solution.

The values of the parameters λ and H are adjustable parameters which could be obtained by the multivariable least squares method [47]. The experimental data and the λH equation model of solubility of 4-position substituted benzoic acid compounds in an aqueous solution are shown in Figures A.5 and A.6. The calculated values of the λH equation model and the percentage of absolute relative deviation (*A.D.* %) are presented in Table A.2. The regression results of the aqueous solubility of 4-position substituted benzoic acid compounds and the values of the parameters λ and H for different systems for the solubility calculations are presented in Table A.4.

Table A.4 The parameters in the λH equation model for different 4-position substituted benzoic acid compounds

Compounds	λH model		
	$\lambda \times 10^3$	$H \times 10^{-3}$	R^2
Benzoic acid	13.94	251.87	0.9920
4-tert-butylbenzoic acid	28.64	1.22	0.9910
4-methylbenzoic acid	35.44	175.61	0.9940
4-formylbenzoic acid	3.90	496.94	0.9940
4-acetylbenzoic acid	9.31	439.82	1.0000
Terephthalic acid	0.20	27119.50	0.9930

A.4.4 Comparison between models

The value of the objective function for correlating the experimental and calculated solubility data of 4-position substituted benzoic acid compounds in an aqueous solution is defined as:

$$A.A.D.(%) = \frac{1}{n} \sum_{i=1}^n \left| \frac{x_e - x_c}{x_e} \times 100 \right| \quad (A.5)$$

where *A.A.D.* (%) is the average absolute relative deviation, x_e is the experimentally measured mole fraction, x_c is the calculated value, and n is the number of experimental points.

The results of the correlation with the modified Apelblat equation model and the λH equation model are shown in Table A.5.

Table A.5 Comparison of the models for the correlation of results of the solubility of 4-position substituted benzoic acid compounds in aqueous solution

Compounds	<i>A.A.D.</i> (%)	
	modified Apelblat model	λH model
Benzoic acid	2.36	1.22
4- <i>tert</i> -butylbenzoic acid	5.69	1.75
4-methylbenzoic acid	8.20	3.29
4-formylbenzoic acid	4.64	3.20
4-acetylbenzoic acid	2.91	1.40
Terephthalic acid	5.09	2.95

Table A.5 shows the values of the objective function for correlating the experimental and calculated solubility data of 4-position substituted benzoic acid compounds in an aqueous solution. The results show that the λH equation model is more suitable for solid-liquid equilibrium systems than the modified Apelblat equation model. The λH equation has the smallest absolute relative deviation of 1.40% for the solubility of 4-acetylbenzoic acid in an aqueous solution and 1.22% for the solubility of benzoic acid in an aqueous solution while the modified Apelblat has the largest value of 8.20% for the solubility of 4-methylbenzoic acid in an aqueous solution. This shows that the λH equation is more applicable than the modified Apelblat equation, with results corresponding to those obtained in the literature [48-50].

A.5 CONCLUSIONS

In this work, the solubility of 4-position substituted benzoic acid compounds in an aqueous solution as a function of temperature was measured within a temperature range of 303.15 to 473.15 K. These data are very helpful not only for industry, but they also form the basis for further theoretical studies.

The solubility data were correlated by empirical formulas, the modified Apelblat equation and λH equation models. The empirical formula model is applicable to regress the aqueous solubility of the above-mentioned compounds, and the squared regression coefficients (R^2) is above 0.99. The maximum percentages of the average absolute relative deviations of the modified Apelblat and λH models were 8.20% and 9.74%, respectively, for the solubility of 4-methylbenzoic acid in an aqueous solution. The minimum percentages of the corresponding average absolute relative deviations of the two models were 2.91% and 1.40% for the solubility of 4-acetylbenzoic acid in an aqueous solution. The deviation calculated by the λH equation model was less than that of the modified Apelblat equation model. The λH equation model can provide a more reasonable prediction for the solute considered. When correlation of the solubility of 4-position substituted benzoic acid compounds in an aqueous solution is required, the λH equation model is preferred because of its simplicity, having two parameters (λ and H) in the equation, and because the best correlation results were obtained.

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APPENDIX B

APPENDIX B

THERMODYNAMICS OF THE SOLUBILITY OF 4-ACETYLBENZOIC
ACID IN DIFFERENT SOLVENTS FROM 303.15 TO 473.15 K

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B.1 ABSTRACT

Solubility data of the solid–liquid equilibrium of 4-acetylbenzoic acid in aqueous and different organic solvents is essential for industrial design and theoretical studies. The solubility of 4-acetylbenzoic acid in water, acetic acid, *p*-cymene, *tert*-butylbenzene, and water-acetic acid (1:1vol.) mixture was measured within a temperature range of 303.15 to 473.15 K. Solubility was measured by the isothermal method and the resulting data were analyzed by regression analysis. The solubility of 4-acetylbenzoic acid was the highest in acetic acid, followed by the water-acetic acid (1:1vol.) mixture, *p*-cymene, *tert*-butylbenzene, then water. The results correlated well with the modified Apelblat equation and the Buchowski–Książczak λH equation. The calculated solubilities by using modified Apelblat solubility model were in good agreement with the experimental data. The percentage of average relative deviations of the correlation is 0.27 for solubility of 4-acetylbenzoic acid in acetic acid solvent.

B.2 INTRODUCTION

Biomass has gained a growing interest in recent years for application as a sustainable and renewable source of chemical precursors [1]. This growing interest for biomass as a resource has captured the interest of many researchers whose main aim is to achieve global sustainability [2]. Consequently, new methods and materials based on biomass refining have emerged for the chemical industry using biomass as feedstock [3]. The concept of developing a biorefinery producing feedstock for the modern chemical industry has been growing in popularity [4]. The conversion of natural biomass materials (e.g., terpenes) to value-added chemicals and fine chemical products is highly important. However, the conversion via catalytic processes remains a considerable challenge [5-7] because biomass materials are a complex mixture including terpenes and terpenoids. Conversion of these compounds to the valuable aromatic compound *p*-cymene is of great commercial interest [8]. Conversion of *p*-cymene to terephthalic acid is achieved by oxidation [9] and several oxidants have been investigated in a preliminary study. The by-products of *p*-cymene oxidation mainly include 4-acetylbenzoic acid (Figure B.1), 4-formylbenzoic acid and 4-isopropyl benzoic acid [10]. Solubility data of the by-products of *p*-cymene oxidation are

important for optimizing the separation of by-products in order to achieve the highest purity of the products of interest.

In the polyester industry, large amounts of oxidation residue are formed during the manufacture of purified terephthalic acid [11, 12]. The by-products of *p*-cymene oxidation, such as 4-acetylbenzoic acid, make up the majority of components in this residue. For the sake of environmental protection and sufficient utilization of natural resources, it is necessary to optimize the separation and recovery of oxidation residues [13]. The solubility of these residues is particularly useful to a wide variety of applications important to the biological, chemical, and environmental industries [14]. Accurate solubility data are required for process and product design including production and purification of chemical compounds [15], separation [16], precipitation [17], crystallization [18], chemical reaction systems [19], pollution prevention [20], and biomass processing [21].

The thermodynamic modeling of experimental solubility data enables researchers to represent mathematical aspects of solubility [22]. A number of methods exist to estimate the solubility of a solute in solvent mixtures [23]. According to these methods, the solubility of a solute can be predicted in different systems [24]. In previous work [25], the modified Apelblat equation [26-28] and Buchowski–Książczak λH equation [29, 30] were applied to predict the solubilities of 4-acetylbenzoic acid in different solvents. In the present work, the solubility of 4-acetylbenzoic acid in different solvents was measured for a temperature range from 303.15 to 473.15 K and the modified Apelblat equation and the Buchowski–Książczak λH equations were used to correlate and predict the solubility data of 4-acetylbenzoic acid. These represent rapid and easy methods to provide acceptable values of solubility as a function of temperature.

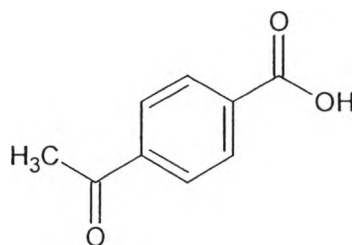


Figure B.1 The structures of 4-acetylbenzoic acid

B.3 EXPERIMENT

B.3.1 Materials

4-acetylbenzoic acid ($C_9H_8O_3$, molecular weight 164.16 g/mol, melting temperature (T_m) = 483.15 K [15]), 1-methyl-4-(1-methylethyl)benzene (*p*-cymene, $C_{10}H_{14}$, molecular weight 134.22 g/mol, density 0.8570 g/mL), (1,1-dimethylethyl)benzene (*tert*-butylbenzene, $C_{10}H_{14}$, molecular weight 134.22 g/mol, density 0.8670 g/mL), and acetic acid ($C_2H_4O_2$, molecular weight 60.05 g/mol, density 1.0490 g/mL) were obtained from Sigma-Aldrich with stated purity of 98% by mass. All solvents used were of GR grade and were purchased from Mikrochem[®], Slovakia. The compounds were used without further purification (Table B.1). The aqueous solutions were prepared using redistilled water.

Table B.1 Solvent properties

Solvent	Properties			Analysis method
	<i>M.W.</i> (g/mol)	<i>D</i> (g/mL)	Purity (%)	
<i>p</i> -cymene	134.22	0.8570	99.90	HPLC
<i>tert</i> -butylbenzene	134.22	0.8670	99.90	HPLC
acetic acid	60.05	1.0490	99.85	HPLC
water	18.02	0.9982	100.00	HPLC

B.3.2. Apparatus and procedures

The solubility of 4-acetylbenzoic acid in different solvents was measured by the isothermal method. The experimental setup scheme is shown in Figure B.2. The solubility experiments were carried out in a 50 mL-stainless steel closed vessel equipped with a magnetic stirrer. 25 mL of the corresponding solvent was put into the vessel to dissolve the acids, which were accurately weighed to the 5th decimal place using a 5-figure analytical balance. The solid-liquid system was mixed sufficiently to allow the experiment to be performed. The vessel was heated in a thermostatic silicone oil bath with an accuracy of ± 0.1 K.

The system was stirred for 90 min (because preliminary results showed this was sufficient time to reach equilibrium) then allowed to stand for 120 min during

which time all suspended particles settled to 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 solution (about 0.5 mL) was captured. To minimize loss of solvents from evaporation during sampling, the valve of the container was quickly closed and the stainless steel vessel was then cooled to ambient temperature by washing with water. After opening the vessel, the closed container was washed three times with 100 mL of distilled water and air dried. The amount of the sample withdrawn into the container was determined as the difference between the weight of the container before and after sampling. After opening the container, the withdrawn sample was transferred into a volumetric flask and after appropriate dilution and interpolation from previously constructed calibration curves for each system, was analyzed by High-performance liquid chromatography (HPLC). The density of the saturated solutions was used to convert from molarity to mole-fraction concentration. The density of the saturated solutions was determined with a digital density meter (LiquiPhysics[™] Excellence Density Meters, Mettler-Toledo, Greifensee, Switzerland).

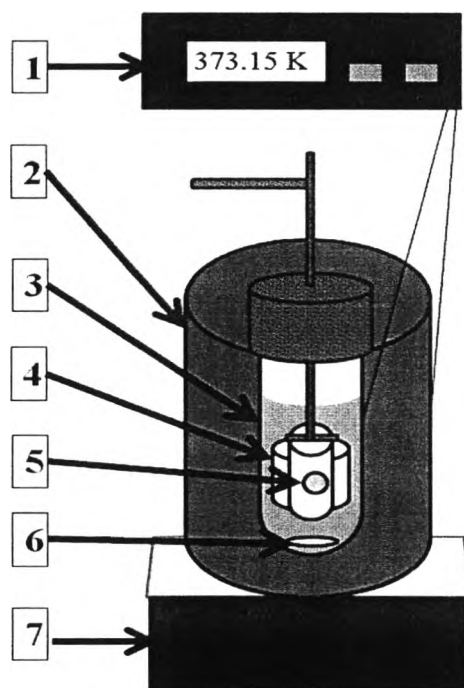


Figure B.2 The experimental apparatus

1. Temperature control 2. Silicone oil bath 3. Stainless steel vessel 4. Teflon[®] container 5. Sampling vessel 6. Magnetic stirrer 7. Stirrer controller

B.3.3 Analytical instruments and chromatographic conditions

The solubility of 4-acetylbenzoic acid was determined by HPLC. The chromatographic system was equipped with a Shimadzu LC10AD high-pressure binary solvent delivery system, using a Rheodyne injector provided with a 20 μL sample loop and a Shimadzu SPD-M10Vp photodiode-array detector. Data analysis was carried out using the Class 10 software for control of the system, data acquisition and integration [31, 32].

The chromatographic procedure was carried out at ambient temperature by using LiChrospher[®] 100 RP-18 e, Merck column (5 μm , 4.0 \times 250 mm). The mobile phase was prepared by mixing monosodium dihydrogen phosphate buffer (10 mmol/L) of pH 1.88 and acetonitrile (40:60 %v/v). The flow rate of the mobile phase was 1.0 mL/min and the injection volume was 20 μL . The sample was detected at 240 nm and the retention time of 4-acetylbenzoic acid was approximately 3.70 min. The measurements were performed in duplicate and the precision of the determination for all derivatives was calculated from triplicate injections. The pH of the aqueous phase was measured with a SevenMulti[™] Modular Expansion pH meter (Mettler-Toledo, Greifensee, Switzerland). All experiments were conducted in triplicate and the mean values were used to calculate the solubility.

B.4 RESULTS AND DISCUSSION

B.4.1 Solubility data

The solubilities of 4-acetylbenzoic acid in water, listed in Table B.2, were measured to complete previously reported data [25]. The measured solubility (Table B.2) differed from the literature values by less than 0.1% [25, 33, 34], verifying the reliability of the experimental apparatus. We validated the experimental measurement of temperature-dependent equilibrium method by comparing the temperature-dependent equilibria [35]. The solubility data of 4-acetylbenzoic acid in water, acetic acid, *p*-cymene, *tert*-butylbenzene, and water-acetic acid (1:1 vol.) mixture are listed in Table B.3, in which T is the absolute temperature and x_e is the experimentally measured mole fraction of 4-acetylbenzoic acid. The equilibrium

solubility of 4-acetylbenzoic acid increased with temperature for each solvent studied. Throughout the temperature range studied, the increasing order of solubility of 4-acetylbenzoic acid in basic solution was: *p*-cymene > *tert*-butylbenzene > acetic acid > water-acetic acid mixture (1:1vol.) > water (Figure B.3).

Table B.2 The mole fraction solubilities (x) of 4-formylbenzoic acid, 4-acetylbenzoic acid and aqueous terephthalic acid compared to literature values

System	T/K	$10^3 x_e$	$10^3 x_{ref}$	$A.D.(%)$
4-formylbenzoic acid in water	353.15	0.3611	0.3608 [33]	0.0831
4-acetylbenzoic acid in water	353.15	0.4769	0.4772 [25]	0.0629
terephthalic acid in water	303.15	0.0073	0.0073 [34]	0.0000

Table B.3 The mole fraction solubilities (x) of 4-acetylbenzoic acid in different solvents at temperatures ranging from 303.15 to 473.15 K

(a) The mole fractions solubilities (x) of 4-acetylbenzoic acid in *p*-cymene

T/K	$10^3 x_e$	$10^3 x_{mA.c.}$	$A.D._{mA.c.}(%)$	$10^3 x_{\lambda H.c.}$	$A.D._{\lambda H.c.}(%)$
453.15	120.6289	119.4644	0.97	129.6460	7.48
443.15	92.0193	91.8870	0.14	94.3489	2.53
433.15	70.4554	70.5190	0.09	71.5621	1.57
423.15	54.1320	54.0038	0.24	55.7234	2.94
413.15	41.1369	41.2715	0.33	41.1469	0.02
403.15	31.3441	31.4801	0.43	31.3769	0.10
393.15	24.1711	23.9685	0.84	24.5558	1.59
383.15	18.2768	18.2197	0.31	19.1454	4.75
373.15	13.9812	13.8302	1.08	14.7907	5.79
363.15	10.4987	10.4859	0.12	10.2482	2.39
353.15	8.0168	7.9435	0.91	8.3448	4.09
343.15	6.0198	6.0144	0.09	5.9538	1.10
333.15	4.5091	4.5534	0.98	4.5803	1.58
323.15	3.4556	3.4487	0.20	3.3512	3.02
313.15	2.6024	2.6147	0.47	2.6092	0.26
303.15	1.9896	1.9859	0.19	1.9840	0.28
$A.A.D. (%)$			<u>0.46</u>		<u>2.47</u>

(b) The mole fractions solubilities (x) of 4-acetylbenzoic acid in *tert*-butylbenzene

T/K	$10^3 x_e$	$10^3 x_{mAc.}$	$A.D._{mAc.}(\%)$	$10^3 x_{\lambda H.c.}$	$A.D._{\lambda H.c.}(\%)$
453.15	114.0306	112.9448	0.95	115.0390	0.88
443.15	87.6669	87.6728	0.01	89.4692	2.06
433.15	67.8516	67.8886	0.05	69.4524	2.36
423.15	51.9784	52.4422	0.89	53.7985	3.50
413.15	39.9911	40.4148	1.06	41.5748	3.96
403.15	30.9724	31.0751	0.33	32.0477	3.47
393.15	23.8652	23.8416	0.10	24.6388	3.24
383.15	18.2169	18.2543	0.21	18.8914	3.70
373.15	13.8375	13.9497	0.81	14.4448	4.39
363.15	10.6298	10.6418	0.11	11.0143	3.62
353.15	8.1671	8.1061	0.75	8.3755	2.55
343.15	6.1757	6.1671	0.14	6.3520	2.85
333.15	4.7283	4.6876	0.86	4.8050	1.62
323.15	3.5661	3.5612	0.14	3.6261	1.68
313.15	2.7089	2.7055	0.13	2.7304	0.79
303.15	2.0545	2.0565	0.10	2.0521	0.12
<i>A.A.D.</i> (%)			<u>0.41</u>		<u>2.55</u>

(c) The mole fractions solubilities (x) of 4-acetylbenzoic acid in acetic acid

T/K	$10^3 x_e$	$10^3 x_{mAc.}$	$A.D._{mAc.}(\%)$	$10^3 x_{\lambda H.c.}$	$A.D._{\lambda H.c.}(\%)$
453.15	58.3287	58.7936	0.80	58.1055	0.38
443.15	47.3118	47.2641	0.10	45.9520	2.87
433.15	37.9555	37.9515	0.01	37.7798	0.46
423.15	30.4722	30.4425	0.10	29.6685	2.64
413.15	24.5262	24.3977	0.52	24.0432	1.97
403.15	19.5253	19.5395	0.07	19.5263	0.01
393.15	15.6704	15.6409	0.19	15.8594	1.21
383.15	12.5292	12.5171	0.10	12.8592	2.63
373.15	10.0503	10.0175	0.33	10.3918	3.40
363.15	8.0674	8.0201	0.59	8.3572	3.59
353.15	6.4363	6.4256	0.17	6.4785	0.66
343.15	5.1512	5.1545	0.06	5.2952	2.80
333.15	4.1584	4.1420	0.39	4.1593	0.02
323.15	3.3182	3.3363	0.55	3.2314	2.62
313.15	2.6943	2.6957	0.05	2.6789	0.57
303.15	2.1786	2.1868	0.38	2.1742	0.20
<i>A.A.D.</i> (%)			<u>0.27</u>		<u>1.63</u>

(d) The mole fractions solubilities (x) of 4-acetylbenzoic acid in water-acetic acid (1:1 vol.) mixture

T/K	$10^3 x_e$	$10^3 x_{mAc}$	$A.D._{mAc}(\%)$	$10^3 x_{\lambda H.c}$	$A.D._{\lambda H.c}(\%)$
453.15	18.7280	18.6763	0.28	18.8437	0.62
443.15	14.7684	14.6513	0.79	14.6837	0.57
433.15	11.5043	11.4878	0.14	11.5018	0.02
423.15	9.0194	9.0046	0.16	9.0273	0.09
413.15	7.0686	7.0578	0.15	7.0806	0.17
403.15	5.5734	5.5331	0.72	5.5378	0.64
393.15	4.3818	4.3402	0.95	4.3103	1.63
383.15	3.4036	3.4078	0.12	3.3326	2.09
373.15	2.6818	2.6793	0.09	2.5552	4.72
363.15	2.1217	2.1106	0.52	2.1394	0.84
353.15	1.6591	1.6667	0.46	1.6546	0.27
343.15	1.3260	1.3204	0.42	1.3263	0.02
333.15	1.0487	1.0501	0.13	0.9841	6.16
323.15	0.8422	0.8393	0.34	0.8312	1.31
313.15	0.6759	0.6748	0.16	0.6394	5.40
303.15	0.5485	0.5465	0.36	0.5270	3.92
<i>A.A.D. (%)</i>			<u>0.36</u>		<u>1.78</u>

(e) The mole fractions solubilities (x) of 4-acetylbenzoic acid in water

T/K	$10^3 x_e$	$10^3 x_{mAc}$	$A.D._{mAc}(\%)$	$10^3 x_{\lambda H.c}$	$A.D._{\lambda H.c}(\%)$
473.15	10.7076	10.7264	0.18	10.0686	5.97
463.15	8.3215	8.3880	0.80	7.9714	4.21
453.15	6.5474	6.5432	0.06	6.3101	3.62
443.15	5.0567	5.0915	0.69	4.9846	1.43
433.15	3.9587	3.9523	0.16	3.9226	0.91
423.15	3.0852	3.0607	0.79	3.0702	0.49
413.15	2.3828	2.3647	0.76	2.3866	0.16
403.15	1.7885	1.8229	1.92	1.8399	2.87
393.15	1.3936	1.4022	0.62	1.4047	0.80
383.15	1.0915	1.0764	1.38	1.0606	2.83
373.15	0.8144	0.8247	1.26	0.7907	2.91
363.15	0.6362	0.6309	0.83	0.5812	8.65
353.15	0.4769	0.4818	1.03	0.4705	1.34
343.15	0.3658	0.3676	0.49	0.3699	1.12
333.15	0.2749	0.2801	1.89	0.2785	1.31
323.15	0.2149	0.2134	0.70	0.2122	1.26
313.15	0.1604	0.1626	1.36	0.1548	3.50
303.15	0.1226	0.1239	1.03	0.1215	0.93
<i>A.A.D. (%)</i>			<u>0.89</u>		<u>2.46</u>

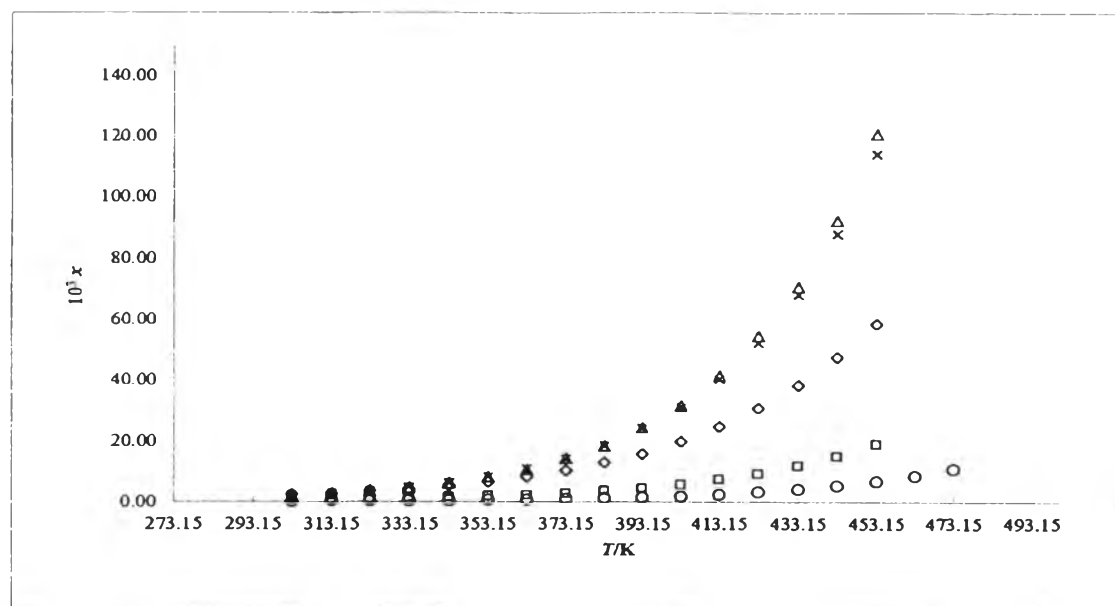


Figure B.3 The mole fractions solubilities (x) of 4-acetylbenzoic acid in different solvents at temperatures from 303.15 to 473.15 K; \triangle 4-acetylbenzoic acid in *p*-cymene; \times 4-acetylbenzoic acid in *tert*-benzene; \diamond 4-acetylbenzoic acid in acetic acid; \square 4-acetylbenzoic acid in water-acetic acid (1:1 vol.) mixture; \circ 4-acetylbenzoic acid in water.

B.4.2 Empirical formula

The solubility is the highest equilibrium concentration of a compound in a solvent at a given temperature. For a given system, the specified temperature is one of the most important and fundamental factors to influence solubility [36]. In this work, an empirical formula represented by Eq. (B.1) was used to calculate the solubility of 4-acetylbenzoic acid. All regression analyses gave correlation coefficients (R^2) greater than 0.99 (Figure B.4) for 4-acetylbenzoic acid. The results shown in figure B.4 indicate that the models obtained adequately describe the experimental data.

$$x_i = K_1 \exp(K_2 T) \quad (\text{B.1})$$

where K_1 and K_2 are the constant parameters for the empirical model.

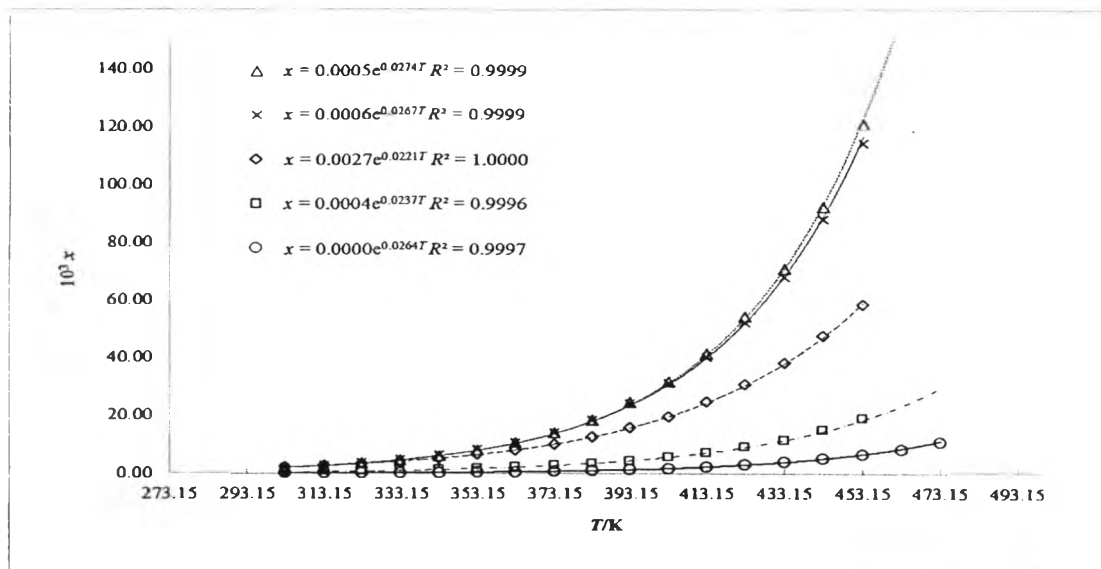


Figure B.4 The mole fractions solubilities (x) and the empirical formula model correlation of 4-acetylbenzoic acid in different solvents at temperatures from 303.15 to 473.15 K; Δ 4-acetylbenzoic acid in *p*-cymene; \times 4-acetylbenzoic acid in *tert*-benzene; \diamond 4-acetylbenzoic acid in acetic acid; \square 4-acetylbenzoic acid in water-acetic acid (1:1 vol.) mixture; \circ 4-acetylbenzoic acid in water.

B.4.3 Thermodynamic model of solubility calculations

In the thermodynamic solubility models, activity coefficients are used to investigate the solid-liquid equilibrium system [37]. According to thermodynamic theory there are many equations generally applied [38], such as the Wilson equation model, the modified Apelblat equation model, the Buchowski–Ksiazczak λH equation model, NRTL, UNIQUAC and UNIFAC. The modified Apelblat equation and the λH equation models have been used to satisfactorily describe experimental data similar to that generated here [25], therefore these two models were selected for use.

B.4.3.1 The modified Apelblat equation

The widely used modified Apelblat model is a semi-empirical model, suitable for nonpolar as well as polar systems. To describe solid–liquid equilibrium, the temperature dependence of the solubilities of 4-acetylbenzoic acid in various solvents at different temperatures can be represented by Eq. (B.2) [39].

$$\ln \frac{1}{\gamma_i x_i} = \frac{\Delta_m H_a^f}{RT_i} \left(\frac{T_i}{T} - 1 \right) - \frac{\Delta C_p}{R} \left(\frac{T_i}{T} - 1 \right) + \frac{\Delta C_p}{R} \ln \left(\frac{T_i}{T} \right) \quad (\text{B.2})$$

where γ_i is the activity coefficient of 4-acetylbenzoic acid on a mole fraction basis, x_i is the mole fraction solubility of 4-acetylbenzoic acid, $\Delta_m H_a^f$ is the enthalpy of fusion of 4-acetylbenzoic acid, ΔC_p is the change of the heat capacity, T is the absolute temperature, T_i is the triple-point temperature of 4-acetylbenzoic acid, and R is the gas constant.

For common solutions, the activity coefficient is given by [40] the following relation:

$$\ln \gamma_i = a + \frac{b}{T} \quad (\text{B.3})$$

where a and b are constants. Introducing γ_i from Eq. (B.3) into Eq. (B.2) and by subsequent rearrangement we obtain Eq. (B.4) which can be written as [41]:

$$\ln x_i = \left[\frac{\Delta_m H_a^f}{RT_i} \left(\frac{T_i}{T} - 1 \right) + \frac{\Delta C_p}{R} (1 + \ln T_i) - a \right] - \left[b + \left(\frac{\Delta_m H_a^f}{RT_i} + \frac{\Delta C_p}{R} \right) T_i \right] \frac{1}{T} - \frac{\Delta C_p}{R} (\ln T) \quad (\text{B.4})$$

Assuming that the enthalpy of the solution is directly proportional to the temperature then from Eq. (B.4), the modified Apelblat equation gives the expression obtained from Clausius-Clapeyron equation [26, 42-44]:

$$\ln x_i = A + \frac{B}{T} + C \ln(T) \quad (\text{B.5})$$

where T is the absolute temperature, and A , B , and C are parameters obtained by fitting the experimental solubility data. Eq. (B.5) is used to correlate the solubility of 4-acetylbenzoic acid in several solvents.

The parameters A , B and C were estimated by correlating the experimental data. The optimum algorithm employed the Nelder-Mead method [45], in which the objective function was the percentage of absolute relative deviation ($A.D.$ (%)) between the experimental and calculated model mole fraction of 4-acetylbenzoic acid. The experimental data, the calculated values and the percentage of absolute relative deviation ($A.D.$ (%)) are presented in Tables B.2 and B.3. The definition of $A.D.$ (%) is given by the following relation:

$$A.D.(%) = \frac{|x_e - x_c|}{x_e} \times 100 \quad (B.6)$$

where x_e is the experimentally measured mole fraction of 4-acetylbenzoic acid, x_c is the value calculated by Eq. (B.5).

The regressed parameter values are listed in Table B.4. The measured data and the modified Apelblat model of aqueous solubility of 4-acetylbenzoic acid in high temperature solutions are shown in Figure B.5. The squared correction coefficients of the regression (R^2) are all greater than 0.99. The regression shows that this model gives a good fit with the experimental data.

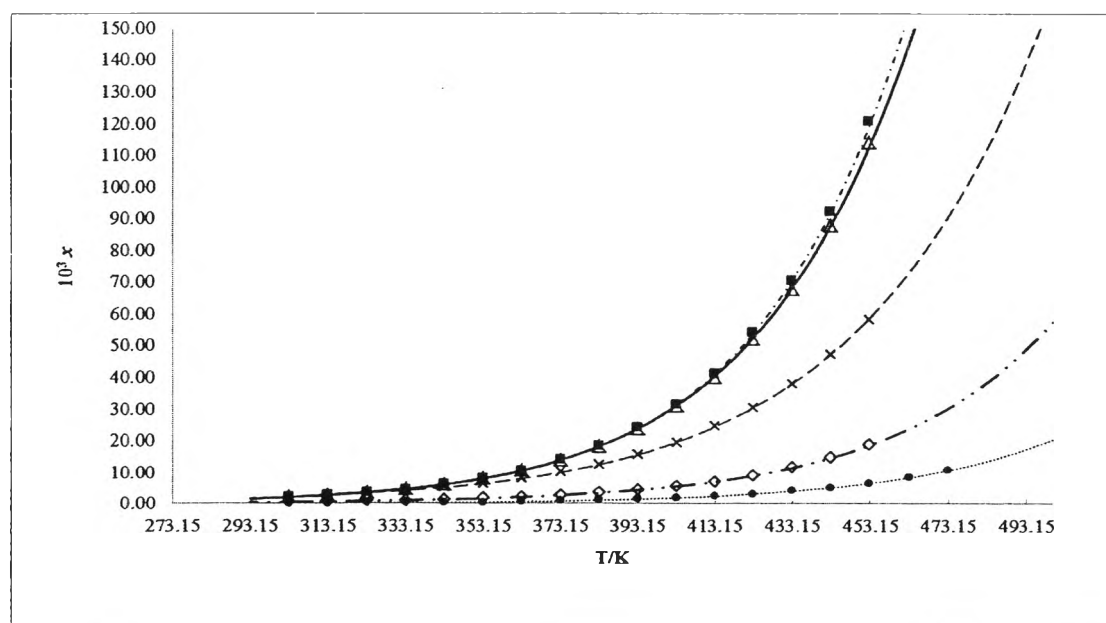


Figure B.5 The mole fractions solubilities (x) and the modified Apelblat model correlation of 4-acetylbenzoic acid in different solvents at temperatures from 303.15 to 473.15 K; ■ 4-acetylbenzoic acid in *p*-cymene; △ 4-acetylbenzoic acid in *tert*-benzene; × 4-acetylbenzoic acid in acetic acid; ◇ 4-acetylbenzoic acid in water-acetic acid (1:1 vol.) mixture; ● 4-acetylbenzoic acid in water;

--- modified Apelblat model-4-acetylbenzoic acid in *p*-cymene;
 ——— modified Apelblat model-4-acetylbenzoic acid in *tert*-benzene;
 - - - modified Apelblat model-4-acetylbenzoic acid in acetic acid;
 - · - modified Apelblat model-4-acetylbenzoic acid in water-acetic acid (1:1 vol.) mixture;
 ····· modified Apelblat model-4-acetylbenzoic acid in water.

Table B.4 The modified Apelblat model parameters for 4-acetylbenzoic acid in different solvents

Solvent	modified Apelblat model			
	A	B	C	R^2
<i>p</i> -cymene	-125.42	3239.20	18.99	0.9990
<i>tert</i> -butylbenzene,	-116.93	2858.70	17.73	0.9990
acetic acid	-114.80	3288.30	17.12	0.9980
water-acetic acid (1:1 vol.) mixture	-138.95	4316.60	20.51	0.9970
water	-118.75	2836.10	17.57	1.0000

B.4.3.2 Buchowski–Książczak equation (λH equation)

The Buchowski–Książczak λH equation (Eq. (B.7)) is an alternative way to describe the solubility behavior. This equation was first suggested by Buchowski et al. [46] to describe the correlation between activity, solubility, and temperature. They found that $\ln(1-a_2)$ is a linear function of the reciprocal of temperature, and consequently deduced the dissolution equation for solid-liquid phase equilibrium of binary systems. The Buchowski–Książczak λH equation has the advantage of having

two adjustable parameters, λ and H , that give it versatility in fitting data for many systems. The λH equation model was selected to fit our experimental data because it is capable of dealing with strong polarity systems, which involve strong interaction between molecules. The Buchowski–Książczak λH equation is as follows:

$$\ln \left[1 + \frac{\lambda(1-x_i)}{x_i} \right] = \lambda H \left[\frac{1}{T} - \frac{1}{T_m} \right] \quad (\text{B.7})$$

where T_m is the normal melting temperature of solute, λ and H are the two equation parameters, and x_i represents the mole fraction of a solute compound in a solvent saturated solution.

The values of the parameters λ and H are adjustable parameters which could be obtained by the multivariable least-square method [47]. The regression results of the aqueous solubility of 4-acetylbenzoic acid and the values of the parameters λ and H for different systems for the solubility calculations are presented in Table B.5. The experimental data and the λH equation model of solubility of 4-acetylbenzoic acid in different solvents are shown in Figure B.6. The calculated values of the λH equation model and the percentage of absolute relative deviation (*A.D.* (%)) are presented in Table B.3. The regression results of the aqueous solubility of 4-acetylbenzoic acid and the values of the parameters λ and H for different systems for the solubility calculations are given in Table B.6.

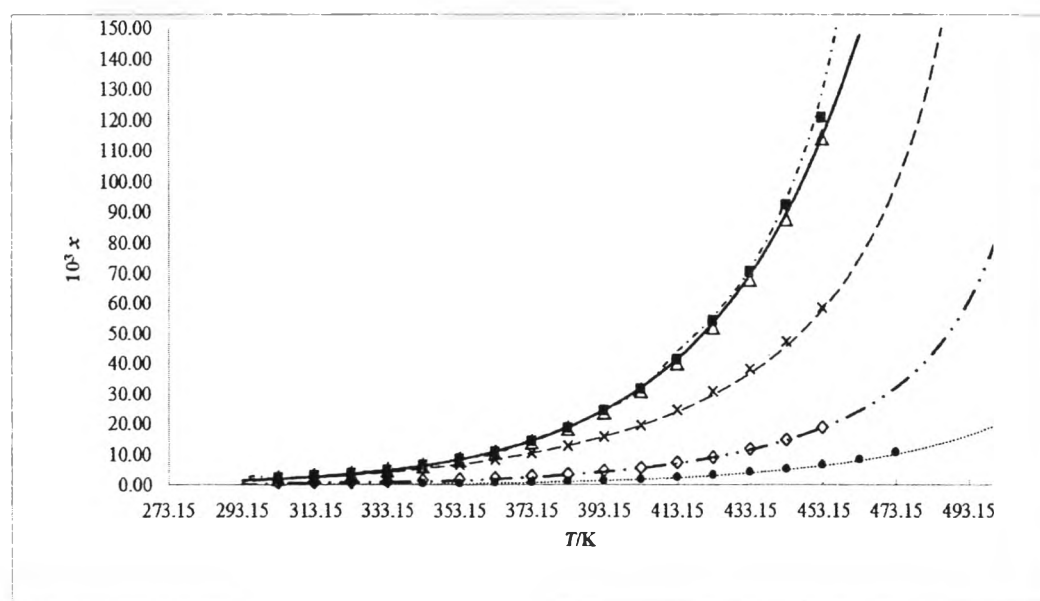


Figure B.6 The mole fractions solubilities (x) and the λH equation model

correlation of 4-acetylbenzoic acid in different solvents at temperatures from 303.15

to 473.15 K; ■ 4-acetylbenzoic acid in *p*-cymene; △ 4-acetylbenzoic acid in *tert*-

benzene; × 4-acetylbenzoic acid in acetic acid; ◇ 4-acetylbenzoic acid in water-

acetic acid (1:1 vol.) mixture; ● 4-acetylbenzoic acid in water;

--- λH model-4-acetylbenzoic acid in *p*-cymene;

— λH model-4-acetylbenzoic acid in *tert*-benzene;

-- λH model-4-acetylbenzoic acid in acetic acid;

-·-· λH model-4-acetylbenzoic acid in water-acetic acid (1:1 vol.) mixture;

····· λH model-4-acetylbenzoic acid in water.

Table B.5 The parameters in the λH equation model for 4-acetylbenzoic acid in different solvents

Solvents	λH model		
	λ	H	R^2
<i>p</i> -cymene	0.045739	47820.72	0.9980
<i>tert</i> -butylbenzene,	0.042173	42168.65	0.9990
acetic acid	0.036581	70114.79	0.9990
water-acetic acid (1:1 vol.) mixture	0.020825	169980.16	0.9980
water	0.009306	439817.82	1.0000

B.4.3.3 Comparison between models

The experimental results are shown in Figures B.5 and B.6. We can observe that the experimental data for 4-acetylbenzoic acid are a good fit for the modified Apelblat and the λH equations. The modified Apelblat equation is considerably better than the λH equation, what is in correspondence with the results obtained by C.L. Zhang et al. [48-50]. The values of the objective function for correlating solubility of 4-acetylbenzoic acid in different solvents were the percentage of average absolute

relative deviation (*A.A.D.* (%)) between the experimental and calculated solubility data of 4-acetylbenzoic acid, which is defined as:

$$A.A.D.(\%) = \frac{1}{n} \sum_{i=1}^n \left| \frac{x_e - x_c}{x_e} \times 100 \right| \quad (\text{B.8})$$

where x_e is the experimentally measured mole fraction of 4-acetylbenzoic acid, x_c is the calculated value and n is the number of experimental points.

The results of the correlation with the modified Apelblat equation model and the λH equation model are shown in table B.6.

Table B.6 Comparison of the model correlation results for the solubility of 4-acetylbenzoic acid in different solvents

Solvent	<i>A.A.D.</i> (%)	
	modified Apelblat model	λH model
<i>p</i> -cymene	0.46	2.47
<i>tert</i> -butylbenzene	0.41	2.55
acetic acid	0.27	1.63
water-acetic acid (1:1 vol.) mixture	0.36	1.78
water	0.89	2.46

The calculated results exhibit that the modified Apelblat equation model has the smallest percentage of A.D. of 0.27% for solubility of 4-acetylbenzoic acid in acetic acid. The λH equation model has the largest value of 2.47% for the solubility of 4-acetylbenzoic acid in different solvents. The data in Table B.6 show that the modified Apelblat equation model is more suitable for describing the solid-liquid equilibrium than the λH equation model. The modified Apelblat equation consistently gave lower A.D. (%) than the λH equation did, consistent with the observations of C.L. Zhang et al. [48-50].

B.4.4 Thermodynamic parameters

The dissolution process of solid (*so*) in liquid (*li*) is a pseudo chemical reaction process [49-51]. The process can be expressed as $so+li = soli$. The relationship of its dissolution equilibrium constants and activities can be expressed as

$$K_i = \frac{a_i}{a_{so}a_{li}} \quad (\text{B.9})$$

where a_i is the activity of 4-acetylbenzoic acid in solution, a_{so} is the activities of pure solid, a_{li} is the activities of pure liquid.

The a_{so} value and a_{li} value are believed almost remain constant in the experimental range because all solid and liquid are in the standard states. The a_{so} value and a_{li} value are considered to be a constant. Therefore, Eq. (B.9) can be written as:

$$K_i = \frac{\gamma_i x_i}{a_{so}a_{li}} \quad (\text{B.10})$$

where γ_i is the activity coefficient of 4-acetylbenzoic acid (i) in the solution on a mole fraction basis, x_i is the mole fraction solubility of 4-acetylbenzoic acid (i) in the solution.

The activity coefficient is invariable during a certain temperature range because of the assumption of the modified Apelblat equation used in the inferential process [52]. Eq. (B.11) is obtained from Eq. (B.10) by taking the log.

$$\ln K_i = \ln x_i + j \quad (\text{B.11})$$

where the j value is a temperature-independent constant, which is defined as:

$$j = \ln \gamma_i - \ln a_{so}a_{li} \quad (\text{B.12})$$

Combining Eq. (B.12) and Eq. (B.11), the γ_i can be merged into $a_{so}a_{li}$, thus:

$$\ln K_i = \ln x_i \quad (\text{B.13})$$

Combining the Gibbs–Helmholtz equation and the modified Van't Hoff

equation [53], the equation for calculating the molar enthalpy of dissolution $\Delta_{\text{sol}}H$ can be obtained:

$$\Delta_{\text{sol}}H = -R \frac{d \ln K_i}{dT^{-1}} \quad (\text{B.14})$$

Substituting Eq. (B.13) into Eq. (B.14), Eq. (B.14) becomes:

$$\Delta_{\text{sol}}H = -R \frac{d \ln x_i}{dT^{-1}} \quad (\text{B.15})$$

From Eq. (B.5) to obtain the derivative and substituting it into Eq. (B.14) gives:

$$\Delta_{\text{sol}}H = RT \left(C - \frac{B}{T} \right) \quad (\text{B.16})$$

According to the fundamental thermodynamic relation [54], the equation for calculate the molar entropy of dissolution $\Delta_{\text{sol}}S$ can be obtained according to:

$$\Delta_{\text{sol}}S = R \left(C - \frac{B}{T} \right) \quad (\text{B.17})$$

where B , and C are parameters of the modified Apelblat equation obtained from Table B.4.

The thermodynamic parameters $\Delta_{\text{sol}}H$ and $\Delta_{\text{sol}}S$ can be calculated from Eqs. (B.9) and (B.10), respectively. The results were shown in Table B.7.

Table B.7 shows that the dissolution of 4-acetylbenzoic acid in each solvent in the experimental temperature range was endothermic ($\Delta_{\text{sol}}H > 0$) because the molar enthalpies were positive. The process is endothermic because the newly formed bond energy of attraction between the particles of the 4-acetylbenzoic acid and the solvent molecules is insufficient to overcome the energy of the original association bonds between solute-solute (4-acetylbenzoic acid) and solvent-solvent in each of the

solvents. A positive enthalpy also shows that dissolution of 4-acetylbenzoic acid is an entropy-driven process. This phenomenon likely results from the different molecular structures and space conformations between solute and solvent. Solvent molecules are strong-association complexes with small molecular dimension [55]. The 4-acetylbenzoic acid molecules likely experienced various forces such as electrostatic forces, hydrogen bonding, hydrophobic interactions, and stereoscopic effects in the dissolving process [54]. The 4-acetylbenzoic acid molecules contain acidic groups (-COOH) and complex groups with different characteristics, such as -COCH₃). These groups allow the dissolving 4-acetylbenzoic acid molecules to disrupt the alignment of solvent molecules, which reduces the degree of order in the system and causes the entropy to increase.

B.5 CONCLUSIONS

In this study, the equilibrium solubility data of 4-acetylbenzoic acid in different solvents (water, acetic acid, *p*-cymene, *tert*-butylbenzene, and a water-acetic acid (1:1 vol.) mixture) at temperatures from 303.15 to 473.15 K were measured. The solubility of 4-acetylbenzoic acid as a mole fraction, increased in the order: *p*-cymene > *tert*-butylbenzene > acetic acid > water-acetic acid (1:1 vol.) mixture > water. Solubility correlates with temperature by empirical formulas, the modified Apelblat equation, and by the Buchowski–Książczak λH equation models. Large regression coefficients, greater than 0.99, showed that the modified Apelblat equation and the λH equation provided good representations of the solubility data. The deviation calculated by the modified Apelblat equation was less than that of the Buchowski–Książczak λH equation. The modified Apelblat equation provides a more reasonable prediction for the solute considered. The solubility data and the correlation equations used in this work can be applied to the separation of 4-acetylbenzoic acid from the reaction mixtures of *p*-cymene oxidation and the purification of terephthalic acid.

Table B.7 The thermodynamic parameters $\Delta_{\text{sol}}H$ and $\Delta_{\text{sol}}S$ for 4-acetylbenzoic acid in different solvents at different temperatures

T/K	Solvents									
	<i>p</i> -cymene		<i>tert</i> -butylbenzene		acetic acid		water-acetic acid (1:1 vol.) mixture		water	
	$\Delta_{\text{sol}}H$ (kJ/mol)	$\Delta_{\text{sol}}S$ (J/mol/K)	$\Delta_{\text{sol}}H$ (kJ/mol)	$\Delta_{\text{sol}}S$ (J/mol/K)	$\Delta_{\text{sol}}H$ (kJ/mol)	$\Delta_{\text{sol}}S$ (J/mol/K)	$\Delta_{\text{sol}}H$ (kJ/mol)	$\Delta_{\text{sol}}S$ (J/mol/K)	$\Delta_{\text{sol}}H$ (kJ/mol)	$\Delta_{\text{sol}}S$ (J/mol/K)
453.15	44.6139	98.4529	43.0303	94.9583	37.1605	82.0048	41.3830	91.3229	42.6154	94.0427
443.15	43.0351	97.1118	41.5563	93.7747	35.7371	80.6434	39.6778	89.5358	41.1547	92.8685
433.15	41.4563	95.7088	40.0822	92.5365	34.3138	79.2191	37.9726	87.6661	39.6939	91.6401
423.15	39.8774	94.2395	38.6081	91.2398	32.8904	77.7276	36.2674	85.7081	38.2331	90.3536
413.15	38.2986	92.6990	37.1341	89.8803	31.4671	76.1638	34.5622	83.6553	36.7724	89.0049
403.15	36.7198	91.0821	35.6600	88.4534	30.0437	74.5224	32.8570	81.5006	35.3116	87.5892
393.15	35.1409	89.3830	34.1859	86.9539	28.6203	72.7975	31.1518	79.2364	33.8508	86.1016
383.15	33.5621	87.5952	32.7118	85.3761	27.1970	70.9826	29.4466	76.8539	32.3901	84.5362
373.15	31.9833	85.7116	31.2378	83.7137	25.7736	69.0704	27.7414	74.3438	30.9293	82.8870
363.15	30.4045	83.7242	29.7637	81.9598	24.3503	67.0529	26.0362	71.6954	29.4685	81.1470
353.15	28.8256	81.6243	28.2896	80.1065	22.9269	64.9212	24.3310	68.8970	28.0078	79.3084
343.15	27.2468	79.4020	26.8156	78.1453	21.5036	62.6652	22.6258	65.9355	26.5470	77.3626
333.15	25.6680	77.0463	25.3415	76.0663	20.0802	60.2738	20.9206	62.7963	25.0862	75.3000
323.15	24.0891	74.5448	23.8674	73.8586	18.6568	57.7343	19.2154	59.4627	23.6254	73.1098
313.15	22.5103	71.8835	22.3933	71.5099	17.2335	55.0327	17.5102	55.9162	22.1647	70.7797
303.15	20.9315	69.0466	20.9193	69.0063	15.8101	52.1528	15.8050	52.1358	20.7039	68.2959

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APPENDIX C

POSTER PRESENTATIONS

- 1) **Sunsandee, N., Somwangthanaroj A., Navasearttavisootr., N.** “Blending uniformity analysis of pharmaceutical powder by near infrared spectroscopy.” The 14th International Conference on Near Infrared Spectroscopy, November 23-27, 2009; Bangkok, Thailand.

ORAL PRESENTATIONS

- 1) **Sunsandee, N., Leepipatpiboon, N., Pancharoen, U.** “Enantioseparation of (*S*)-amlodipine by stripping phase recognition via a hollow fiber supported liquid membrane” The 22nd TIChE National Conference and the 2nd TIChE Interational Conference, October 25-26, 2012; Nakhonratchasima, Thailand.
- 2) **Sunsandee, N., Leepipatpiboon, N., Pancharoen, U.** “Enantioselective separation of (*S*)-amlodipine from pharmaceutical industry wastewater by using synergistic selector and specific stripping phase via HFSLM” The 2013 International Conference on Life Science & Biological Engineering (LS&BE 2013), March 15-17, 2013; Tokyo, Japan.

RESEARCH IN FOREIGN LABORATORY

March, 2012 – September, 2012 The Laboratory Catalyzed Processes, Department of Organic Technology, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Slovak Republic with Professor D.Sc. Ing. Milan Hronec.

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PEER REVIEWED JOURNAL PUBLICATIONS**PUBLISHED**

- 1) **Sunsandee, N.**, Pancharoen, U., Rashatasakhon P., Ramakul, P., Leepipatpiboon, N. Enantioselective separation of racemic amlodipine by two-phase chiral extraction containing *O,O'*-dibenzoyl-(2*S*,3*S*)-tartaric acid as chiral selector. Sep. Sci. Technol. (in-press).
- 2) **Sunsandee, N.**, Leepipatpiboon, N., Ramakul, P., Pancharoen, U. The selective separation of (*S*)-amlodipine via a hollow fiber supported liquid membrane: modeling and experimental verification. Chem. Eng. J. 180 (2012): 299-308.
- 3) **Sunsandee, N.**, Ramakul, P., Thamphiphit, N., Pancharoen, U., Leepipatpiboon, N. The synergistic effect of selective separation of (*S*)-amlodipine from pharmaceutical wastewaters via hollow fiber supported liquid membrane. Chem. Eng. J. 209 (2012): 201-214.
- 4) **Sunsandee, N.**, Suren, S., Leepipatpiboon, N., Hronec, M., Pancharoen, U. Determination and modeling of aqueous solubility of 4-position substituted benzoic acid compounds in a high-temperature solution. Fluid Phase Equilib. 338 (2013): 217-223.
- 5) **Sunsandee, N.**, Hronec, M., Štolcová, M., Leepipatpiboon, N., Pancharoen, U. Thermodynamics of the solubility of 4-acetylbenzoic acid in different solvents from 303.15 to 473.15 K. J. Mol. Liq. 180 (2013): 252-259.
- 6) **Sunsandee, N.**, Leepipatpiboon, N., Ramakul, P., Wongsawa, T., Pancharoen, U. The effects of thermodynamics on mass transfer and enantioseparation of (*R,S*)-amlodipine across a hollow fiber supported liquid membrane. Sep. Purif. Technol. 102 (2013): 50-61.
- 7) **Sunsandee, N.**, Ramakul, P., Pancharoen, U., Leepipatpiboon, N. Enantioseparation of (*S*)-amlodipine from pharmaceutical industry wastewater by stripping phase recovery via HFSLM: polarity of diluent and membrane stability investigation. Sep. Purif. Technol. (in-press).
- 8) Naksang, C., **Sunsandee, N.**, Thamphiphit, N., Pancharoen, U., Ramakul, P., Leepipatpiboon, N. Synergistic Enantioseparation of rac-Phenylalanine via Hollow Fiber Supported Liquid Membrane. Sep. Sci. Technol. 48, (2013): 867–876.

- 9) Ramakul, P., Yanachawakul, Y., Leepipatpiboon, N., **Sunsandee, N.** Biosorption of palladium (II) and platinum (IV) from aqueous solution using tannin from Indian almond (*Terminalia catappa* L.) leaf biomass: Kinetic and equilibrium studies. Chem. Eng. J. 193–194 (2012): 102-111.

SUBMITTED

- 1) **Sunsandee, N.**, Ramakul, P., Hronec, M., Pancharoen, U., Leepipatpiboon, N. Mathematic model and experimental validation of synergistic effect of selective enantioseparation of (*S*)-amlodipine from pharmaceutical wastewater by using HFSLM. J. Ind. Eng. Chem. (Submitted).
- 2) Wongsawa, T., **Sunsandee, N.**, Pancharoen, U., Lothongkum, A.W. High efficiency HFSLM for silver ion pertraction from pharmaceutical wastewater and mass transport models. Chem. Eng. Res. Des. (Submitted).
- 3) Suren, S., **Sunsandee, N.**, Hronec, M., Pancharoen, U. Measurement and correlation of solubility of 4-alkyl benzoic acids in different solvents. J. Chem. Eng. Data (Submitted).
- 4) Suren, S., **Sunsandee, N.**, Štolcová, M., Hronec, M., Pancharoen, U. Measurement of the solubility of adipic acid in different solvents at high temperature and thermodynamic modeling. J. Chem. Thermodyn. (Submitted).

IN PREPARATION

- 1) **Sunsandee, N.**, Ramakul, P., Pancharoen, U., Leepipatpiboon, N. Selective enantioseparation of racemic amlodipine by biphasic recognition chiral separation system. (In preparation).
- 2) **Sunsandee, N.**, Ramakul, P., Pancharoen, U., Leepipatpiboon, N. Synergistic enantioseparation of levocetirizine via hollow fiber supported liquid membrane. (In preparation).
- 3) Pirom, T., Wongkaew, K., **Sunsandee, N.**, Pancharoen, U., Leepipatpiboon, N. Simultaneous separation of cobalt and manganese using D2EHPA via a hollow fiber supported liquid membrane: correlation and experimental verification. (In preparation).

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Publications in this dissertation:

1. **Sunsandee, N.,** Pancharoen, U., Rashatasakhon P., Ramakul, P., Leepipatpiboon, N. Enantioselective separation of racemic amlodipine by two-phase chiral extraction containing *O,O'*-dibenzoyl-(2*S*,3*S*)-tartaric acid as chiral selector. Sep. Sci. Technol. (in-press).
2. **Sunsandee, N.,** Leepipatpiboon, N., Ramakul, P., Pancharoen, U. The selective separation of (*S*)-amlodipine via a hollow fiber supported liquid membrane: modeling and experimental verification. Chem. Eng. J. 180 (2012): 299-308.
3. **Sunsandee, N.,** Ramakul, P., Thamphiphit, N., Pancharoen, U., Leepipatpiboon, N. The synergistic effect of selective separation of (*S*)-amlodipine from pharmaceutical wastewaters via hollow fiber supported liquid membrane. Chem. Eng. J. 209 (2012): 201-214.
4. **Sunsandee, N.,** Leepipatpiboon, N., Ramakul, P., Wongsawa, T., Pancharoen, U. The effects of thermodynamics on mass transfer and enantioseparation of (*R,S*)-amlodipine across a hollow fiber supported liquid membrane. Sep. Purif. Technol. 102 (2013): 50-61.
5. **Sunsandee, N.,** Ramakul, P., Pancharoen, U., Leepipatpiboon, N. Enantioseparation of (*S*)-amlodipine from pharmaceutical industry wastewater by stripping phase recovery via HFSLM: polarity of diluent and membrane stability investigation. Sep. Purif. Technol. (in-press).