

1 Solubility of Benzoic Acid in Six Alcohols within (288.15 to 336.15) K 2 and Thermodynamic Properties in the Dissolution Process

3 **Abstract:** The solubility of benzoic acid was determined in six alcohols (isobutanol,
4 *n*-pentanol, isoamylol, 2-pentanol, tert-amyl alcohol and *n*-hexanol) from (288.15 to 336.15) K
5 by dynamic method. The value of solubility rises with the increase of temperature and the
6 order of solvents is tert-amyl alcohol > 2-pentanol > *n*-hexanol > *n*-pentanol > isoamylol >
7 isobutanol. The modified Apelblat equation, λh model, NRTL model and Wilson model were
8 adopted to correlate the experimental data of benzoic acid. The results show the solubilities
9 calculated by the models are consistent with the experimental ones and the modified Apelblat
10 equation gives the best correlation results with the overall relative average deviation 0.60%.
11 Meanwhile the changes of thermodynamic properties of solution, standard molar enthalpy
12 $\Delta_{\text{dis}}H^{\circ}$, standard molar entropy $\Delta_{\text{dis}}S^{\circ}$ and standard molar Gibbs energy $\Delta_{\text{dis}}G^{\circ}$ were
13 calculated with the NRTL model. According to the results, the dissolution of benzoic acid in
14 six alcohols is endothermic and entropy-driven.

15 **Keywords:** Benzoic acid; Solubility; Thermodynamic; Correlation; Dissolution

16 1. Introduction

17 The solubility of solids in the solvent is one of essential physical properties and can be
18 applied to study the industrial crystallization separation process, the mechanism of mass
19 transfer and chemical design and development [1]. For example, the solubility of solids in the
20 solvent plays an important role in choosing the appropriate solvent and operation temperature
21 for the recrystallization. However, the solubility of organic solids in a limited temperature

range is not perfect enough to meet the requirement of large scale industry separation [2]. Therefore, it is necessary to select appropriate thermodynamic model to correlate the solubility data measured by the accurate experiments.

Benzoic acid ($C_7H_6O_2$, CAS Registry No.65-85-0) is a colorless crystalline solid which is one of the most important organic raw materials and products. It is widely used as pharmaceutical intermediates, food additives and cosmetics [3]. In order to obtain the product of benzoic acid with high purity, solution crystallization is regarded as the final purification step in industrial production [4,5]. On the other hand, benzoic acid is often reacted with alcohols to produce benzoic acid esters which are high additional value products that can be used as perfume agent, plasticizer and solvent. And these production processes involve the separation of benzoic acid from alcohols which also needs a lot of solubility data at different temperature. So it is necessary for us to study the solubility of benzoic acid in the alcohols with a wide temperature range based on the importance of solubility of benzoic acid. Systematic experimental solubility data of benzoic acid in methanol, ethanol, *n*-propanol, isopropanol and butanol have been reported [6-9]. Meanwhile the solubilities of benzoic acid in isobutanol, *n*-pentanol and *n*-hexanol at 298.15 K have been determined [10,11]. However the solubility of benzoic acid in *n*-pentanol from Restaino [10] is much higher than that from Charlisa [11] with the relative deviation of 23.36%. Moreover, there are no systematic experimental solubility data of benzoic acid in other alcohols such as isoamylol and tert-amyl alcohol. Therefore further investigation is still needed.

In this paper, the solubility of benzoic acid in isobutanol, *n*-pentanol, isoamylol, 2-pentanol, tert-amyl alcohol and *n*-hexanol was determined within (288.15 to 336.15) K by dynamic method [12,13] and was correlated by the modified Apelblat equation, the λh model, the NRTL model and the Wilson model. Then the standard molar enthalpy ($\Delta_{\text{dis}} H^\circ$), standard molar entropy ($\Delta_{\text{dis}} S^\circ$) and standard molar Gibbs energy ($\Delta_{\text{dis}} G^\circ$) for the dissolving process of benzoic acid in six alcohols were calculated from the experimental data.

2. Experimental

2.1 Materials

Benzoic acid was purchased from Shanghai Ling Feng Chemical Reagent Co., Ltd. And its purity is 0.999 by mass. The solvents, *n*-propanol, isobutanol, *n*-pentanol, isoamylol, *n*-hexanol, 2-pentanol and tert-amyl alcohol involved in the experiments were analytical reagent grade with mass fraction above 0.995. All the information of materials is showed in Table 1.

Table 1. Information of Materials Used

chemical name	source	mass fraction purity	analysis method	purification method
benzoic acid	Ling Feng Chemical Reagent Co., Ltd	> 0.995	HPLC ^a	none
<i>n</i> -propanol	Meryer Co., Ltd., Shanghai, China	> 0.995	GC ^b	none
isobutanol	Meryer Co., Ltd., Shanghai, China	> 0.995	GC ^b	none
<i>n</i> -pentanol	Meryer Co., Ltd., Shanghai, China	> 0.995	GC ^b	none
isoamylol	Meryer Co., Ltd., Shanghai, China	> 0.995	GC ^b	none
2-pentanol	Aladdin Co., Ltd., Shanghai, China	> 0.995	GC ^b	none
tert-Amyl alcohol	Macklin Co., Ltd., Shanghai, China	> 0.995	GC ^b	none
<i>n</i> -hexanol	Meryer Co., Ltd., Shanghai, China	> 0.995	GC ^a	none

^a High performance liquid chromatography
^b Gas chromatography

56

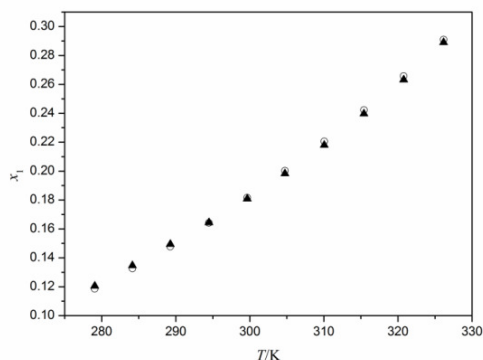
2.2 Apparatus and Procedure

57

58 The determination of solubility of the solute in solvents is generally acquired by
59 gravimetric or dynamic method. In this work, the last solid disappearance method which is a
60 kind of dynamic methods was adopted to determine the solubility of benzoic acid in six pure
61 alcohols. The details of equipment and procedure in our laboratory were included in our
62 previous reported literature [14-17]. It can be described in brief below: A certain mass of
63 solvent (about $20\text{g} \pm 0.001\text{g}$) was added into three-necked flask with agitation equipment and
64 mercury thermometer with standard uncertainty of 0.05 K. Meanwhile a condenser was
65 equipped and all ports tightly sealed to avoid the evaporation of the solvent. A cylindrical
66 glass thermostatic water bath was applied to keep the temperature stable. A certain mass of
67 benzoic acid was added into the flask under a certain temperature, and the mass was
68 measured using the electronic balance (standard uncertainty of 0.0001 g). If the solid
69 previously added completely dissolved which could be judged by whether the solution was
70 clear and colorless or cloudy, then another known mass of solute was added into flask again.
71 Repeated this step until the solution turned cloudy with the last added solid was less than 0.05
72 g and it remained partially undissolved over 3h. Three parallel experiments were performed
73 to reduce experimental accidental error, and the molar solubility was calculated by the mean
74 value of the data. When the data at a constant temperature have been recorded, then raised the
75 temperature and repeated process to acquire solubility at different temperature.

76 In order to check the reliability of the apparatus, the solubilities of benzoic acid were
77 measured in *n*-propanol and the results were presented in Fig. 1. The relative deviations

78 between the experimental data and the ones in literature [6] are all less than 2%, indicating
79 that the solubility data determined with this apparatus are reliable.



80

81 **Fig. 1** The solubility of benzoic acid in *n*-propanol: ▲, experiment data; ○, literature data[6];

82 The molar fraction solubility was calculated by the following expression

83
$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2}$$

84 (1)

85 where x_1 represents the saturated molar fraction of benzoic acid, m_1 and m_2 represent the
86 mass of solute and solvent respectively and M_1 and M_2 represent the molecular mass of
87 solute and solvent respectively. The deviation of the solubility because of the uncertainty of
88 the measurement of weight and temperature along with the purity of the solute and solvent is
89 less than 2%.

90 3. Results and Discussion

91 3.1 Correlation of Solubility

In this work, four solubility models, the modified Apelblat equation, the λh model, the NRTL model and the Wilson model, were adopted to correlate the experimental solubility data. The parameters of these models were acquired by least square method.

3.1.1 Modified Apelblat Equation

The modified Apelblat equation [18,19] is assumed that there is a linear relationship between the mole enthalpy of solution and temperature. The equation can be derived from Clausius-Clapeyron equation [20,21] as follows

$$\ln x_1 = A + \frac{B}{T} + C \ln(T) \quad (2)$$

where A , B , and C are the model parameters which can be achieved by multivariate regression analysis. The parameters A , B indicate the non-idealities of the real solution and C demonstrates the relationship between the fusion enthalpy and temperature.

3.1.2 λh model

The λh model [22,23] also known as Buchowski-Ksiazczak equation, including two adjustable parameters λ and h , is derived from the equation firstly put forward by Buchowski *et al* [24].

$$\ln \left(1 + \lambda \frac{1-x_1}{x_1} \right) = \lambda h \left(\frac{1}{T} - \frac{1}{T_m} \right) \quad (3)$$

In order to clarify the relationship among solubility and temperature more intuitively, Eq. (3) can be deformed into the following form

$$x_1 = \frac{\lambda}{e^{\lambda h \left(\frac{1}{T} - \frac{1}{T_m} \right)} - 1 + \lambda} \quad (4)$$

Where λ can be seen as the non-ideal prosperity of the most solid-liquid equilibrium system and h represents the excess mixing enthalpy of solution. T_m is the melting point of the solute and in this article T_m of benzoic acid is 395.52 K[7].

3.1.3 Activity coefficient model

An activity coefficient model was usually used to correlate solubility based on excess Gibbs energy [25]. And the rigorous thermodynamics equation of this model can be given as follow when the solid is completely pure and the triple point temperature of the solute is approximately equal to the melting temperature [26]:

$$\ln \gamma_1 x_1 = \frac{\Delta_{\text{fus}} H_m}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) - \frac{1}{RT} \int_{T_m}^T \Delta C_p dT + \frac{1}{R} \int_{T_m}^T \frac{\Delta C_p}{T} dT \quad (5)$$

where R is the universal gas constant. ΔC_p is defined as the difference of molar heat capacity between the melting and solid state of solute and $\Delta_{\text{fus}} H_m$ denotes the melting enthalpy of the solute. According to the literature [7], the values of ΔC_p and $\Delta_{\text{fus}} H_m$ of benzoic acid are 57.86 J/(mol • K) and 18006 J/mol respectively. The NRTL model and Wilson model are two common expression chosen for strongly non-ideal binary mixtures.

(1) NRTL model The NRTL model was developed by Renon and Prausnitz [27] based on the non random parameters considering the existence of local composition and shown as follows

$$\ln \gamma_1 = x_2^2 \left[\frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (6)$$

with

$$G_{12} = \exp(-\alpha_{12} \tau_{12}) \quad (7)$$

$$G_{21} = \exp(-\alpha_{21} \tau_{21}) \quad (8)$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} = \frac{\Delta g_{12}}{RT}$$

(9)

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} = \frac{\Delta g_{21}}{RT}$$

(10)

where Δg_{12} , Δg_{21} are two parameters which can be regressed by the experimental data . α is the reflection of the nonrandomness of the solution with $\alpha_{12} = \alpha_{21}$ and its value is suggested from 0.2 to 0.47 [25,28]. In this paper, α_{12} was treated as a constant and its value was 0.3.

(2) Wilson model The Wilson model was proposed by Wilson [29] considering the conception of local composition to correlate the solid-liquid equilibrium and the equation is presented as follows

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right) \quad (11)$$

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) = \frac{V_2}{V_1} \exp\left(-\frac{\Delta\lambda_{12}}{RT}\right) \quad (12)$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) = \frac{V_1}{V_2} \exp\left(-\frac{\Delta\lambda_{21}}{RT}\right) \quad (13)$$

where $\Delta\lambda_{12}$ and $\Delta\lambda_{21}$ are two adjustable parameters which mean the cross interaction energy only related to temperature. V_1 , V_2 are the molar volumes of solute and solvent which could be found from Hansen's handbook [30].

3.2 Solubility Data of Benzoic Acid

The solubility of benzoic acid was measured in six alcohols (isobutanol, *n*-pentanol, isoamylol, 2-pentanol, tert-amyl alcohol and *n*-hexanol) within (288.15 to 336.15) K at 4K interval and the results are listed in Table 2. The experimental data are correlated by the four models based on *Matlab software R2016a* (MathWorks Inc.), and the regression parameters of the models were listed in Table 3. According to the parameters, the calculated solubility data of benzoic acid in six alcohols are also listed in Table 2.

Table 2. Experimental (x_1^{exp}) and Calculated (x_1^{cal}) Molar Fraction Solubility of Benzoic Acid in Six Alcohols From (288.15 to 336.15) K at Pressure $p=0.1$ MPa

T / K	x_1^{exp}	Apelblat	λh	NRTL	Wilson	x_1^{exp}	Apelblat	λh	NRTL	Wilson
isobutanol					<i>n</i> -pentanol					
288.15	0.1257	0.1293	0.1299	0.1315	0.1315	0.1653	0.1670	0.1619	0.1635	0.1631
292.15	0.1405	0.1410	0.1414	0.1425	0.1425	0.1778	0.1773	0.1743	0.1752	0.1750
296.15	0.1550	0.1535	0.1537	0.1543	0.1544	0.1899	0.1886	0.1874	0.1878	0.1876
300.15	0.1689	0.1668	0.1669	0.1670	0.1670	0.2020	0.2009	0.2014	0.2012	0.2011
304.15	0.1838	0.1810	0.1809	0.1806	0.1806	0.2153	0.2143	0.2161	0.2155	0.2155
308.15	0.1974	0.1962	0.1959	0.1951	0.1951	0.2293	0.2290	0.2318	0.2307	0.2308

312.15	0.2113	0.2123	0.2119	0.2106	0.2106	0.2433	0.2451	0.2483	0.2470	0.2472
316.15	0.2293	0.2295	0.2289	0.2277	0.2277	0.2595	0.2626	0.2659	0.2645	0.2647
320.15	0.2467	0.2477	0.2472	0.2460	0.2460	0.2814	0.2816	0.2845	0.2834	0.2836
324.15	0.2662	0.2671	0.2666	0.2658	0.2658	0.3040	0.3024	0.3043	0.3037	0.3039
328.15	0.2855	0.2876	0.2874	0.2870	0.2870	0.3268	0.3251	0.3252	0.3254	0.3255
332.15	0.3079	0.3093	0.3096	0.3102	0.3101	0.3501	0.3498	0.3475	0.3485	0.3485
336.15	0.3353	0.3323	0.3334	0.3358	0.3358	0.3758	0.3768	0.3712	0.3733	0.3732
	<i>RAD</i>	0.0084	0.0085	0.0103	0.0103	<i>RAD</i>	0.0050	0.0117	0.0082	0.0087
isoamylol					2-pentanol					
288.15	0.1444	0.1481	0.1445	0.1463	0.1461	0.1807	0.1830	0.1837	0.1851	0.1856
292.15	0.1583	0.1589	0.1567	0.1579	0.1577	0.1953	0.1955	0.1960	0.1967	0.1971
296.15	0.1724	0.1706	0.1697	0.1703	0.1702	0.2096	0.2087	0.2089	0.2092	0.2094
300.15	0.1863	0.1833	0.1836	0.1836	0.1836	0.2240	0.2226	0.2226	0.2224	0.2226
304.15	0.2001	0.1970	0.1983	0.1978	0.1978	0.2386	0.2372	0.2370	0.2365	0.2366
308.15	0.2135	0.2120	0.2140	0.2129	0.2130	0.2536	0.2527	0.2523	0.2516	0.2515
312.15	0.2274	0.2283	0.2306	0.2291	0.2292	0.2692	0.2689	0.2684	0.2675	0.2673
316.15	0.2428	0.2459	0.2483	0.2466	0.2467	0.2857	0.2860	0.2854	0.2846	0.2842
320.15	0.2632	0.2651	0.2672	0.2657	0.2658	0.3032	0.3040	0.3034	0.3027	0.3022
324.15	0.2847	0.2859	0.2872	0.2863	0.2864	0.3217	0.3229	0.3224	0.3220	0.3214
328.15	0.3090	0.3085	0.3086	0.3086	0.3086	0.3413	0.3428	0.3426	0.3426	0.3418
332.15	0.3336	0.3329	0.3313	0.3324	0.3324	0.3622	0.3636	0.3640	0.3646	0.3636
336.15	0.3603	0.3595	0.3555	0.3581	0.3580	0.3882	0.3855	0.3867	0.3881	0.3868
	<i>RAD</i>	0.0087	0.0104	0.0081	0.0083	<i>RAD</i>	0.0044	0.0047	0.0062	0.0056
tert-amyl alcohol					<i>n</i> -hexanol					
288.15	0.2355	0.2351	0.2310	0.2152	0.2205	0.1728	0.1760	0.1715	0.1729	0.1723
292.15	0.2430	0.2446	0.2424	0.2287	0.2329	0.1861	0.1867	0.1840	0.1848	0.1844
296.15	0.2530	0.2549	0.2543	0.2429	0.2461	0.1997	0.1983	0.1973	0.1976	0.1973
300.15	0.2662	0.2662	0.2669	0.2578	0.2601	0.2134	0.2109	0.2113	0.2112	0.2111
304.15	0.2792	0.2785	0.2801	0.2737	0.2751	0.2268	0.2246	0.2262	0.2256	0.2257
308.15	0.2945	0.2917	0.2940	0.2903	0.2910	0.2405	0.2395	0.2419	0.2410	0.2412
312.15	0.3079	0.3061	0.3086	0.3081	0.3080	0.2543	0.2557	0.2585	0.2575	0.2577
316.15	0.3214	0.3217	0.3240	0.3269	0.3260	0.2713	0.2733	0.2761	0.2750	0.2754
320.15	0.3374	0.3385	0.3403	0.3467	0.3452	0.2912	0.2923	0.2948	0.2938	0.2941
324.15	0.3556	0.3566	0.3576	0.3675	0.3655	0.3127	0.3130	0.3145	0.3139	0.3142
328.15	0.3758	0.3762	0.3759	0.3894	0.3870	0.3353	0.3354	0.3354	0.3354	0.3355
332.15	0.3964	0.3972	0.3952	0.4126	0.4098	0.3615	0.3597	0.3576	0.3585	0.3584
336.15	0.4204	0.4199	0.4158	0.4370	0.4339	0.3851	0.3860	0.3811	0.3829	0.3826
	<i>RAD</i>	0.0034	0.0056	0.0342	0.0264	<i>RAD</i>	0.0061	0.0095	0.0069	0.0078

Standard uncertainties u are $u(T)=0.05\text{K}$, $u_r(P)=0.05$, $u_r(x_i)=0.02$.

159 **Table 3. Parameters of Four Models for Solubility of Benzoic Acid in Six Alcohols**

	Apelblat			λh		NRTL		Wilson	
	A	B	C	λ	h	Δg_{12}	Δg_{21}	$\Delta \lambda_{12}$	$\Delta \lambda_{21}$
isobutanol	-22.9750	-634.9527	4.0846	0.5131	3081.6752	2175.2172	-567.3014	-339.3616	1940.4870
<i>n</i> -pentanol	-120.3974	4090.1910	18.4362	0.4654	2797.2943	2874.3431	-1574.9792	-897.4016	2280.7601
isoamylol	-98.1878	2936.9890	15.2001	0.5289	2847.1347	2050.1562	-786.1027	-192.2154	1472.4124
2-pentanol	-33.7584	215.6157	5.5287	0.3660	2800.2235	4115.1618	-2475.3382	-1722.6272	3912.9031
tert-Amyl alcohol	-107.3384	3899.9857	16.3073	0.1570	2842.9308	-2728.7760	3467.2435	51666.2956	-2916.7790
<i>n</i> -hexanol	-108.9167	3611.2300	16.7118	0.4451	2737.0414	3142.0720	-1873.4232	-936.4284	2543.5345

160 The fitting degree of the data was assessed by the relative average deviation (*RAD*)
 161 calculated by the following formulas and the results are also given in Table 2.

$$162 \quad RAD = \frac{1}{N} \sum_{i=1}^N \left| \frac{x_{1,i}^{\text{exp}} - x_{1,i}^{\text{cal}}}{x_{1,i}^{\text{exp}}} \right| \quad (14)$$

163 where $x_{1,i}^{\text{exp}}$ means experimental data while $x_{1,i}^{\text{cal}}$ is the fitted data. N is the number of
 164 experimental points.

165 The experimental and calculated solubilities of benzoic acid in isobutanol, tert-amyl alcohol
 166 and *n*-hexanol within (288.15 to 336.15) K are plotted in Fig. 2. From Table 2 and Fig. 2, the
 167 conclusion can be drawn that the solubility of benzoic acid in six alcohols increases with the
 168 increase of temperature and satisfies the order of tert-amyl alcohol > 2-pentanol >
 169 *n*-hexanol > *n*-pentanol > isoamylol > isobutanol. The polarity order of six solvents is
 170 *n*-pentanol > isoamylol > *n*-hexanol > isobutanol > 2-pentanol > tert-Amyl alcohol [31],
 171 which is not well consistent with the solubility order. These results indicate that not only

172 polarity but also other factors such as inter-molecular interaction can affect the solubility [32].
173 The activity coefficient γ_1 can be calculated by the NRTL model to estimate the solute-solvent
174 inter-molecular interactions. The larger activity coefficient of benzoic acid means the weaker
175 solute-solvent interactions and stronger homo-molecules interactions. And the stronger
176 solute-solvent interaction is more favorable for the dissolution process. The plots of γ_1
177 versus T for six alcohols are shown in Fig. 3. From Fig. 3, the order of the activity coefficient
178 is tert-amyl alcohol < 2-pentanol < *n*-hexanol < *n*-pentanol < isoamylol < isobutanol, which
179 means the increasing homo-molecules interactions and decreasing solute-solvent interactions.
180 The trend is consist with the solubility order, which indicates that the inter-molecular
181 interaction is the main factor for the solubility of benzoic acid in the solvents. Meanwhile the
182 overall *RADs* of these four models are all less than 2% which means the experimental data
183 match well with the chosen model. The modified Apelblat equation gives the best correlation
184 results (the overall *RADs* 0.60%) among the four models.

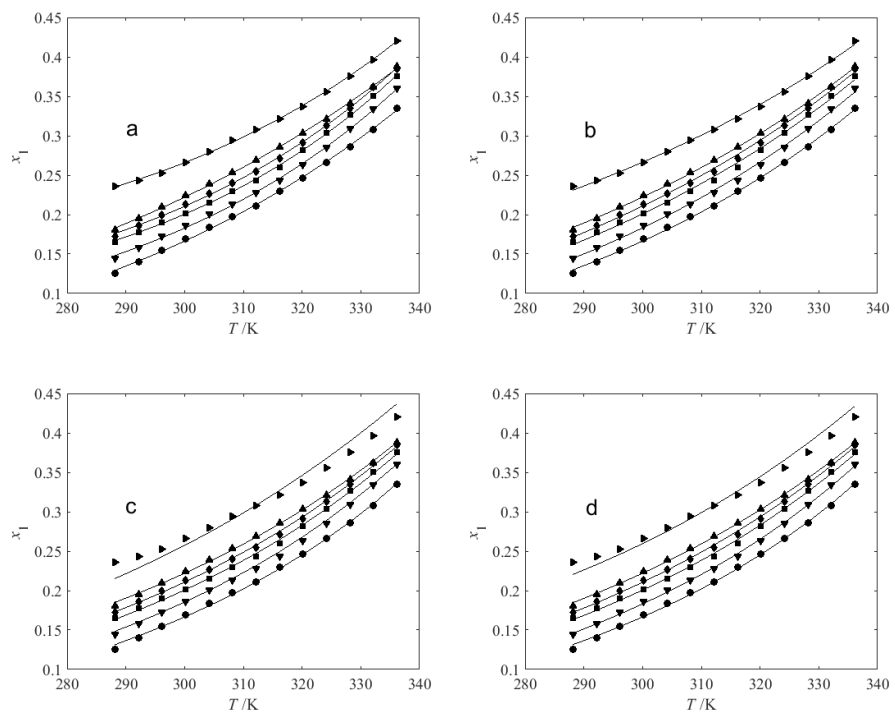


Fig. 2 Solubility of benzoic acid by molar fraction in six alcohols: ●, isobutanol; ▼, isoamylol; ■, *n*-pentanol; ◆, *n*-hexanol; ▲, 2-pentanol; ►, tert-amyl alcohol; -, thermodynamic model: a, modified Apelblat equation; b, λh model; c, NRTL model; d, Wilson model.

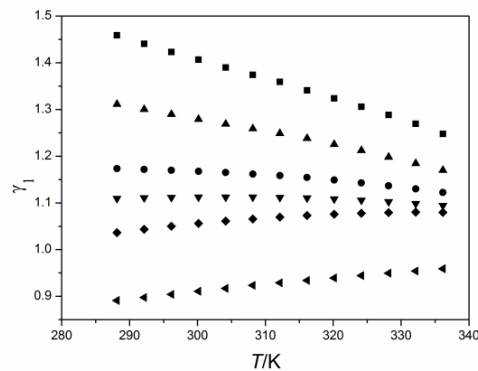


Fig. 3 The activity coefficient of benzoic acid based on NRTL model in six solvents: ■, isobutanol; ▲, isoamylol; ●, *n*-pentanol; ▼, *n*-hexanol; ◆, 2-pentanol; ◄, tert-Amyl alcohol;

the solubility of benzoic acid in *n*-pentanol and *n*-hexanol at 298.15 K was predicted by the modified Apelblat equation and the comparison between them and the ones in literature [10,11] is presented in Fig. 4. From Fig. 4, the predicted solubility in *n*-hexanol is in agreement with the value by Restaino [10] with the relative deviation 1.6%, and the predicted solubility in *n*-pentanol is between the two literature values with the relative deviations of -16.1% [10] and 5.9% [11] respectively.

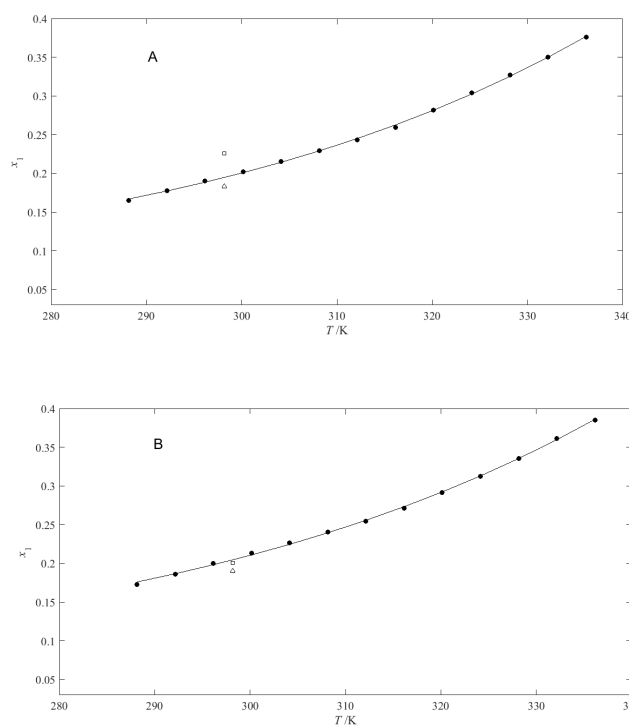


Fig. 4 Comparison between experimental and literature data of solubility of benzoic acid in different solvents at 298.15 K: ●, experiment data; □, literature data[10]; Δ, literature data[11]; –, calculated from the modified Apelblat equation. (A) *n*-pentanol; (B) *n*-hexanol

3.3 Thermodynamic properties of solution

All the dissolution processes are accompanied by the changes of thermodynamic functions which include enthalpy ($\Delta_{\text{dis}}H^{\circ}$), entropy ($\Delta_{\text{dis}}S^{\circ}$) and Gibbs free energy ($\Delta_{\text{dis}}G^{\circ}$). In order to get a better understanding of the dissolution process of benzoic acid in selected alcohols, the thermodynamic parameters need to be calculated. The parameters $\Delta_{\text{dis}}H^{\circ}$, $\Delta_{\text{dis}}S^{\circ}$, and $\Delta_{\text{dis}}G^{\circ}$ of the dissolution process of benzoic acid can be calculated according to the following hypothetical process and Eqs. (15) to (17) [33]. The dissolution process can be divided into two independent processes, fusion and mixing, so the changes of thermodynamic functions can be the sum of the two parts.



$$\Delta_{\text{dis}}H^{\circ} = \Delta_{\text{fus}}H^{\circ} + \Delta_{\text{mix}}H^{\circ} \quad (15)$$

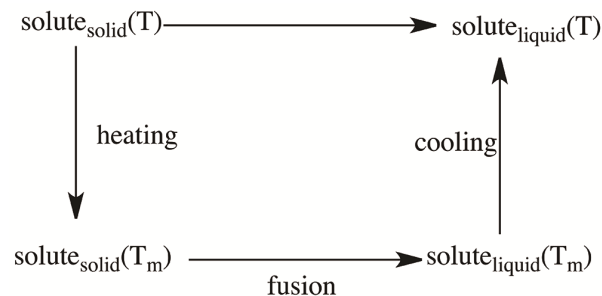
$$\Delta_{\text{dis}}S^{\circ} = \Delta_{\text{fus}}S^{\circ} + \Delta_{\text{mix}}S^{\circ} \quad (16)$$

$$\Delta_{\text{dis}}G^{\circ} = \Delta_{\text{fus}}G^{\circ} + \Delta_{\text{mix}}G^{\circ} \quad (17)$$

where $\Delta_{\text{fus}}H^{\circ}$, $\Delta_{\text{fus}}S^{\circ}$, and $\Delta_{\text{fus}}G^{\circ}$ mean the changes of enthalpy, entropy, and Gibbs energy in fusion process while $\Delta_{\text{mix}}H^{\circ}$, $\Delta_{\text{mix}}S^{\circ}$, and $\Delta_{\text{mix}}G^{\circ}$ are the changes of enthalpy, entropy and Gibbs energy in mixing process.

According to Scheme 1, $\Delta_{\text{fus}}H^{\circ}$, $\Delta_{\text{fus}}S^{\circ}$ and $\Delta_{\text{fus}}G^{\circ}$ can be calculated from Eqs. (18) to (20).

Scheme 1. Thermodynamic Cycle for Fusion



224

225
$$\Delta_{\text{fus}} H^{\circ} = C_{\text{p},\text{solid}}(T_{\text{m}} - T) + \Delta_{\text{fus}} H_{\text{m}}^{\circ} + C_{\text{p},\text{liquid}}(T - T_{\text{m}}) = \Delta_{\text{fus}} H_{\text{m}}^{\circ} + \Delta C_{\text{p}}(T - T_{\text{m}}) \quad (18)$$

226
$$\Delta_{\text{fus}} S^{\circ} = C_{\text{p},\text{solid}} \ln \frac{T_{\text{m}}}{T} + \Delta_{\text{fus}} S_{\text{m}}^{\circ} + C_{\text{p},\text{liquid}} \ln \frac{T}{T_{\text{m}}} = \Delta_{\text{fus}} S_{\text{m}}^{\circ} + \Delta C_{\text{p}} \ln \frac{T}{T_{\text{m}}} \quad (19)$$

227
$$\Delta_{\text{fus}} G^{\circ} = \Delta_{\text{fus}} H^{\circ} - T \Delta_{\text{fus}} S^{\circ} \quad (20)$$

228 where $C_{\text{p},\text{solid}}$ and $C_{\text{p},\text{liquid}}$ represent heat capacity of solute in solid state and liquid state,

229 respectively. $\Delta_{\text{fus}} S_{\text{m}}^{\circ}$ is fusion entropy of solute and the equation which can be used to

230 calculate $\Delta_{\text{fus}} S_{\text{m}}^{\circ}$ is given as follows

231
$$\Delta_{\text{fus}} S_{\text{m}}^{\circ} = \frac{\Delta_{\text{fus}} S_{\text{m}}^{\circ}}{T_{\text{m}}} \quad (21)$$

232 The results of $\Delta_{\text{fus}} H^{\circ}$, $\Delta_{\text{fus}} S^{\circ}$ and $\Delta_{\text{fus}} G^{\circ}$ of benzoic acid were listed in Table 4.

233 **Table 4. Thermodynamic Properties of Fusion Process for Benzoic Acid**

T/K	$\Delta_{\text{fus}} H^{\circ} / (\text{J} \cdot \text{mol}^{-1})$	$\Delta_{\text{fus}} S^{\circ} / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	$\Delta_{\text{fus}} G^{\circ} / (\text{J} \cdot \text{mol}^{-1})$
288.15	11794	27.20	3956
292.15	12025	28.00	3846
296.15	12256	28.78	3732
300.15	12488	29.56	3615
304.15	12719	30.33	3496
308.15	12951	31.08	3373
312.15	13182	31.83	3247
316.15	13414	32.57	3118
320.15	13645	33.29	2986
324.15	13877	34.01	2852
328.15	14108	34.72	2714

332.15	14339	35.42	2574
336.15	14571	36.11	2431

234

235 For a real solution, the changes of thermodynamic properties in a mixing process can be
236 calculated by the following expression [34,35]

$$237 \quad \Delta_{\text{mix}} H^o = \Delta_{\text{mix}} H^{\text{id}} + H^E \quad (22)$$

$$238 \quad \Delta_{\text{mix}} G^o = \Delta_{\text{mix}} G^{\text{id}} + G^E \quad (23)$$

$$239 \quad \Delta_{\text{mix}} S^o = \Delta_{\text{mix}} S^{\text{id}} + S^E \quad (24)$$

$$240 \quad \text{Here, } \Delta_{\text{mix}} H^{\text{id}} = 0 \quad (25)$$

$$241 \quad \Delta_{\text{mix}} G^{\text{id}} = RT(x_1 \ln x_1 + x_2 \ln x_2) \quad (26)$$

$$242 \quad \Delta_{\text{mix}} S^{\text{id}} = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad (27)$$

$$243 \quad H^E = -T^2 \left[\frac{\partial (G^E/T)}{\partial T} \right] \quad (28)$$

$$244 \quad G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (29)$$

$$245 \quad S^E = \frac{H^E - G^E}{T} \quad (30)$$

246 Where superscript *id* and *E* represent the property of ideal solution and the excess property
247 respectively. The parameters γ_1 and γ_2 are obtained from the calculation of NRTL model .

248 The thermodynamic properties of benzoic acid in six alcohols were calculated and listed in
249 Table 5. In addition, the relative contributions of enthalpy and entropy to the Gibbs free
250 energy in the dissolution process, can be compared by the parameters $\zeta_H\%$ and $\zeta_S\%$ and
251 the expressions of these two parameters were shown below

$$\xi_H \% = \frac{|\Delta_{\text{dis}} H^o|}{|\Delta_{\text{dis}} H^o| + |T \Delta_{\text{dis}} S^o|} \times 100 \quad (31)$$

$$\xi_S \% = \frac{|T \Delta_{\text{dis}} S^o|}{|\Delta_{\text{dis}} H^o| + |T \Delta_{\text{dis}} S^o|} \times 100 \quad (32)$$

Table 5. Dissolution Thermodynamic Properties of Benzoic Acid in Six Alcohols

<i>T</i> /K	$\Delta_{\text{dis}} H^o$ /(J•mol ⁻¹)	$\Delta_{\text{dis}} S^o$ /(J•K ⁻¹ •mol ⁻¹)	$\Delta_{\text{dis}} G^o$ /(J•mol ⁻¹)	% ξ_H	% ξ_S	$\Delta_{\text{dis}} H^o$ /(J•mol ⁻¹)	$\Delta_{\text{dis}} S^o$ /(J•K ⁻¹ •mol ⁻¹)	$\Delta_{\text{dis}} G^o$ /(J•mol ⁻¹)	% ξ_H	% ξ_S
isobutanol						<i>n</i> -pentanol				
288.15	11872	30.18	3175	57.72	42.28	11763	30.59	2949	57.17	42.83
292.15	12113	31.20	2998	57.06	42.94	11996	31.54	2782	56.56	43.44
296.15	12355	32.19	2822	56.45	43.55	12229	32.46	2615	55.99	44.01
300.15	12596	33.15	2646	55.87	44.13	12463	33.37	2445	55.44	44.56
304.15	12837	34.10	2466	55.31	44.69	12697	34.28	2271	54.91	45.09
308.15	13078	35.01	2289	54.79	45.21	12931	35.17	2092	54.4	45.60
312.15	13319	35.91	2109	54.30	45.70	13166	36.05	1913	53.92	46.08
316.15	13563	36.84	1917	53.80	46.20	13401	36.93	1726	53.44	46.56
320.15	13805	37.73	1727	53.34	46.66	13638	37.83	1527	52.97	47.03
324.15	14049	38.62	1531	52.88	47.12	13874	38.71	1328	52.51	47.49
328.15	14292	39.48	1337	52.45	47.55	14112	39.56	1131	52.09	47.91
332.15	14537	40.34	1137	52.04	47.96	14350	40.39	935	51.68	48.32
336.15	14783	41.21	932	51.63	48.37	14589	41.20	739	51.30	48.70
isoamylol						2-pentanol				
288.15	11850	30.47	3071	57.44	42.56	11606	30.45	2832	56.95	43.05
292.15	12088	31.46	2898	56.81	43.19	11831	31.40	2658	56.33	43.67
296.15	12327	32.43	2723	56.21	43.79	12057	32.32	2484	55.74	44.26
300.15	12565	33.38	2547	55.64	44.36	12284	33.23	2309	55.19	44.81
304.15	12803	34.30	2371	55.10	44.90	12512	34.13	2133	54.66	45.34
308.15	13041	35.20	2193	54.59	45.41	12741	35.01	1954	54.15	45.85
312.15	13280	36.09	2013	54.10	45.90	12971	35.87	1774	53.67	46.33
316.15	13519	36.98	1828	53.63	46.37	13202	36.73	1590	53.20	46.80
320.15	13759	37.89	1630	53.15	46.85	13433	37.57	1405	52.76	47.24
324.15	14000	38.78	1431	52.69	47.31	13665	38.40	1218	52.33	47.67
328.15	14242	39.66	1228	52.25	47.75	13899	39.22	1029	51.92	48.08
332.15	14484	40.51	1027	51.84	48.16	14133	40.02	840	51.53	48.47
336.15	14725	41.35	826	51.44	48.56	14369	40.82	647	51.15	48.85
tert-amy alcohol						<i>n</i> -hexanol				

288.15	11520	31.06	2571	56.28	43.72	11717	31.02	2897	56.73	43.27
292.15	11749	31.92	2423	55.75	44.25	11947	31.56	2727	56.44	43.56
296.15	11976	32.80	2264	55.22	44.78	12179	32.50	2555	55.86	44.14
300.15	12204	33.68	2094	54.69	45.31	12410	33.42	2380	55.30	44.70
304.15	12432	34.55	1923	54.19	45.81	12642	34.31	2206	54.78	45.22
308.15	12661	35.42	1745	53.70	46.30	12875	35.20	2029	54.28	45.72
312.15	12890	36.26	1571	53.24	46.76	13108	36.06	1851	53.80	46.20
316.15	13119	37.08	1395	52.81	47.19	13342	36.94	1663	53.32	46.68
320.15	13348	37.91	1213	52.38	47.62	13576	37.81	1470	52.86	47.14
324.15	13578	38.72	1026	51.96	48.04	13810	38.67	1274	52.42	47.58
328.15	13809	39.53	837	51.56	48.44	14046	39.52	1078	52.00	48.00
332.15	14041	40.32	649	51.18	48.82	14282	40.35	880	51.59	48.41
336.15	14274	41.09	460	50.82	49.18	14519	41.15	688	51.21	48.79

255

256 The values of $\zeta_H\%$ and $\zeta_S\%$ were also listed in Table 5. Considering all the values of
257 $\Delta_{\text{dis}}H^\circ$ and $\Delta_{\text{dis}}S^\circ$ are positive, the dissolution processes of benzoic acid in six alcohols are
258 endothermic and entropy-driven. Moreover, the values of $\Delta_{\text{dis}}G^\circ$ decrease with the increase
259 of temperature. In these systems, enthalpy is the major contributor to the dissolution of Gibbs
260 free energy due to all values of $\zeta_H\%$ in this work more than 50%.

261 4. Conclusion

262 The solubilities of benzoic acid were determined in isobutanol, *n*-pentanol, isoamylol,
263 2-pentanol, tert-amyl alcohol and *n*-hexanol within (288.15 to 336.15) K, and they increase
264 when the temperature increases. The decreasing order of solubility is tert-amyl alcohol >
265 2-pentanol > *n*-hexanol > *n*-pentanol > isoamylol > isobutanol and is in reverse order of the
266 activity coefficient which indicates that the main effect of the solubility is inter-molecular
267 interaction. The modified Apelblat Equation, the λh model, the NRTL model and the Wilson

model were used to correlate the above experimental data. The results show that all these models have a good agreement with the the experimental data because the overall *RADs* of them were 0.60% (modified Apelblat equation), 0.84% (λh model) , 1.23% (NRTL model) , 1.12% (Wilson model), respectively. So the experimental data and calculated data correlated by the selected models in this work can be of great benefit for purifying benzoic acid from alcohols in industrial production. Besides the thermodynamic properties of solution involved standard molar enthalpy $\Delta_{\text{dis}}H^{\circ}$, standard molar entropy $\Delta_{\text{dis}}S^{\circ}$ and standard molar Gibbs energy $\Delta_{\text{dis}}G^{\circ}$ were calculated with the NRTL model and the dissolution process of benzoic acid in these solvents proves to be endothermic and entropy-driven according to the results.

References

- [1] Bhattachar. Shobha N, Deschenes. Laura A, Wesley. James A, Drug Discov Today. 11 (2006) 1012-1018.
- [2] Y. D. Zhang, J. Chem. Eng. Data. 56 (2011) 2403-2406.
- [3] S Budavari, The Merck Index, an encyclopedia of chemical drug, and biologicals, MerckCo. Inc, Nanjing, 1996.
- [4] M. Barrett, M. McNamara, H. Hao, B. Glennon, Chem. Eng. Res. Des. 88 (2010) 1108–1119.
- [5] D. O’Grady, M. Barrett, E. Casey, B. Glennon, Chem. Eng. Res. Des. 85 (2007) 945–952.
- [6] T Gavin, G. Y. Hou, G Brian, J. Chem. Eng. Data. 61 (2016) 594–601.
- [7] B. Long, R. Zhang, L. Wan, Fluid Phase Equilib. 297 (2010) 113–120.

- 288 [8] R. F. Pires, J. M. R. Franco, J. Chem. Eng. Data. 53 (2008) 2704-2706.
- 289 [9] S. Zhao, X. Chen, Q. Dai, L. Wang, J. Chem. Eng. Data. 56 (2011) 2399–2402.
- 290 [10] F. A. Restaino, A. N. Martin, J. Pharm. Sci. 53 (1964) 636-639.
- 291 [11] Daniels. Charlisa R, Charlton. Amanda K, Phys. Chem. Liq. 41 (2003) 599-603.
- 292 [12] S. Black, L. P. Dang, C. J. Liu, H. Y. Wei, Org. Process Res. Dev. 17 (2013) 486–492.
- 293 [13] P. J. Gandhi, Z. V. P. Murthy, J. Chem. Eng. Data. 55 (2010) 5050-5054.
- 294 [14] C. Yu, Z. X. Zeng, W. L. Xue, Ind. Eng. Chem. Res. 54 (2015) 3961–3967.
- 295 [15] C. Yu, Z. J. Huang, Z. X. Zeng, W. L. Xue, J. Solution Chem. 45 (2016) 395-409.
- 296 [16] J. Chen, Z. X. Zeng, W. L. Xue, D. Wang, Y. Huang, Ind. Eng. Chem. Res. 50 (2011)
- 297 11755-11762.
- 298 [17] X. Gao, Z. X. Zeng, W. L. Xue, X. R. Fan, J. Chem. Eng. Data. 60 (2015) 2273-2279.
- 299 [18] F. Shakeel, G. A. Shazly, Haq. N, J. Chem. Eng. Data. 59 (2014) 1700-1703.
- 300 [19] F. Shakeel, M. A. Bhat, Haq. N, J. Chem. Eng. Data. 59 (2014) 2660-2664.
- 301 [20] Alexander Apelblat, Emanuel Manzurola, J. Chem. Thermodyn. 33 (2001) 147 -153.
- 302 [21] Alexander Apelblat, Emanuel Manzurola, J. Chem. Thermodyn. 31 (1999) 85-91.
- 303 [22] M. H. Hong, S. W. Wu, M. H. Qi, G. B. Ren, Fluid. Phase. Equilibr. 409 (2016) 1-6.
- 304 [23] A. Noubigh, A. Aydi, M. Abderrabba, J. Chem. Eng. Data. 60 (2015) 514-518.
- 305 [24] H. Buchowski, A. Ksiazczak, S. Pietrzyk, J. Phys. Chem. 84 (1980) 975-979.
- 306 [25] G. M. Yu, L. S. Wang, J. Sun, L. K. Jiang, J. Chem. Eng. Data. 60 (2015) 1803-1813.
- 307 [26] J. M. Prausnitz., R. N. Lichtenthaler., E. G. D. Azevedo, Molecular Thermodynamics of
- 308 Fluid Phase Equilibria, Prentice-Hall, NewYork, 1999.

- 309 [27] H. Renon, J. M. Prausnitz, *AIChE J.* 14 (1968) 135-144.
- 310 [28] D. W. Wei, Y. H. Pei, *Ind. Eng. Chem. Res.* 47 (2008) 8953-8956.
- 311 [29] G. M. Wilson, *J. Am. Chem. Soc.* 86 (1964) 127-130.
- 312 [30] C. M. Hansen, *Hansen solubility parameters: a user's handbook*, CRC Press, New York,
- 313 2007.
- 314 [31] I. M. Smallwood, *Handbook of Organic Solvent Properties*, Arnold, London, 1996.
- 315 [32] W. Tang, H. Dai, Y. Feng, S. Wu, Y. Bao, J. Wang and J. Gong, *J. Chem. Thermodyn.*
- 316 90 (2015) 28-38.
- 317 [33] C. Wang, Y. L. Wang, Q. X. Yin, Z. Xu, Y. Bao, B. H. Hou, W. Liu, H. X. Hao, J.
- 318 *Chem. Eng. Data.* 60 (2015) 3053-3061.
- 319 [34] G. Q. Zhou, C. B. Du, S. Han, L. Meng, J. Wang, R. R. Li, H. K. Zhao, *J. Chem.*
- 320 *Thermodyn.* 90 (2015) 259-269.
- 321 [35] J. M. Smith., H. C. V. Ness., M. M. Abbott, *Introduction to Chemical Engineering*
- 322 *Thermodynamics*, McGraw-Hill, New York, 2001.
- 323