



Chemical Engineering Thermodynamics

Measurement and correlation of solubility of trimethylolethane in different pure solvents and binary mixtures☆



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ABSTRACT

The solubilities of trimethylolethane in butanol, methyl acetate, ethyl acetate as well as in mixed solvents of (methanol + ethyl acetate) and (ethanol + ethyl acetate) were measured with the gravimetric method in the temperature range from 283.15 K to 318.15 K under atmosphere pressure. The experiment results showed that the solubility of trimethylolethane increased with the temperature, or along with the concentration of methanol or ethanol in the solvents of (methanol + ethyl acetate) and (ethanol + ethyl acetate). In addition, the experiment values were correlated by the van't Hoff equation, Modified Apelblat Equation, λh Equation, CNIBS/R-K equation and Jouyban–Acree Model. The Modified Apelblat Equation provided the best fitting results of the solubility data of TME in the pure solvents while the CNIBS/R-K model showed the best estimation of the solubility in the binary solvent mixtures. Furthermore, the density functional theory (DFT) calculations showed that solubility in different solvents related to the strength of the interaction between the trimethylolethane and the solvent molecules. Finally, the standard molar enthalpy and molar entropy of trimethylolethane during the dissolving process was also calculated by Modified Apelblat equation in this work.

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1. Introduction

Trimethylolethane ($C_5H_{12}O_3$, CAS registry No. 77-85-0), a crystalline solid polyhydric alcohol with molar mass of $120.15 \text{ g} \cdot \text{mol}^{-1}$, is an important intermediate to synthesize resins, lubricants, plasticizers, stabilizers for plastics and new industrial explosive [1,2]. In particular, the mixture of trimethylolethane and polyhydric alcohol is a promising high-density phase change material slurries used in the heat storage equipment [3]. However, the small amount of impurities existed in trimethylolethane (TME) can make the performance of the following TME-associated product deteriorated greatly [4].

Extraction and crystallization are the popular industrial operation process to purify TME [5–7], which needs the solubility data of trimethylolethane in different solvents. In particular, the solubility in mixed solvents is fundamental to develop an effective technology manufacturing high-purity TME. So far, no experimental solubility data of TME in binary mixed solvents have been found in the open literature.

In this work, the solubility data of TME in some pure alcohol and acetate solvents, as well as those in the ethyl acetate-associated binary solvent mixtures were measured in the temperature range from 283.15 K to 318.15 K, with the gravimetric method. The experimental solubility data were then correlated by van't Hoff equation, modified Apelblat equation, λh Equation, Jouyban–Acree equation and CNIBS/R-K equation. To interpret the solubility behavior of TME in the selected solvent, dissolution molar enthalpy change and entropy change were also calculated by van't Hoff equation.

2. Experimental

2.1. Materials

Trimethylolethane, as is shown in Fig. 1, was purchased from Tianjin Xiensibiochemical technology co., LTD, China. It was recrystallized twice in pure ethanol. The final mass fraction of TME measured by gaschromatography (SP-2100A Beifen-Ruili) was higher than 0.995. Methanol (mass fraction purity of 0.998), ethanol (mass fraction purity of 0.998), butanol (mass fraction purity of 0.995), ethyl acetate (mass fraction purity of 0.998) and methyl acetate (mass fraction purity of 0.998) were purchased from Tianjin Guangfu Fine Chemical Research Institute, China. The water used in all experiments was distilled three times.

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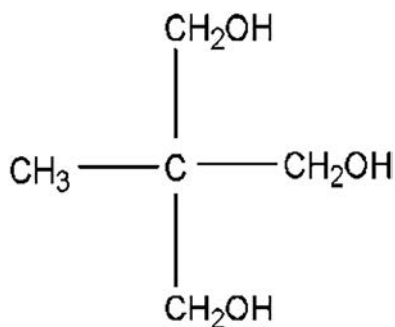


Fig. 1. Chemical structure of trimethylolethane.

2.2. Thermal analysis

The melting points and enthalpy of fusion ΔH_{fus} of TME were studied by a TGA/DSC simultaneous thermal analyzer (Model TGA/DSC, Mettler-Toledo, Switzerland) under the protection of a flowing nitrogen atmosphere. The heating rate was $5 \text{ K} \cdot \text{min}^{-1}$.

2.3. X-ray power diffraction

X-ray powder diffraction spectrum of the sample was performed on XRD equipment (WRS-1B, Shanghai precision scientific instrument co., LTD) with $\text{Cu K}\alpha$ radiation (0.071073 nm) in the 2-theta range of 15° to 50° with scanning rate of $4^\circ \cdot \text{min}^{-1}$. PXRD patterns of TME used in the experiment are presented in Fig. 2, which is in agreement with the standard pattern.

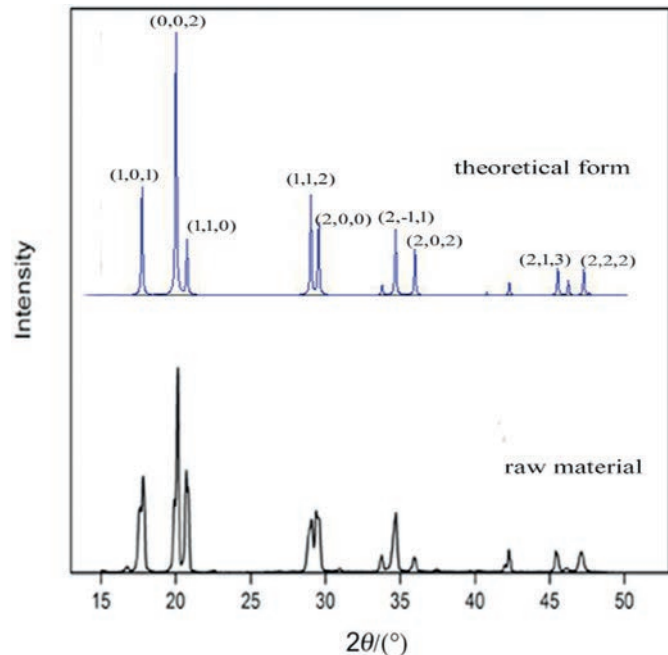


Fig. 2. X-ray powder diffraction patterns of TME.

2.4. Solubility measurements

The solubility of TME in butanol, methyl acetate, ethyl acetate, methanol-ethyl acetate mixtures and ethanol-ethyl acetate mixtures was determined by gravimetric method [8–10] in the temperature ranging from 283.15 K to 318.15 K . The experimental apparatus contains a

conical flask and a shaking table (Tianjin Ounuo Instrument Co., LTD, China) with an uncertainty of $\pm 0.1 \text{ K}$. Before all the experiments, three mercury thermometers were put at different places in the shaking table to calibrate the temperature of thermostat within shaking table. At first, excessive amounts of dried TME were added into the solvents, then the equilibrium cell was heated to the desired temperature and was shaken for 12 h, which was enough for the phase equilibrium. After that, another 12 h was taken to make sure that the excess solute settles down under the same temperature. The equilibrium was verified by measuring the concentration value of supernate at different time intervals until the concentration reached the constant. Then the supernatant was transferred rapidly into the vial with a cover and was weighed immediately with an analytical balance (Startorius scientific instrument co., LTD, Beijing) to obtain the total weight, then the vial containing the solution was dried carefully in an air oven (Beijing ever light medical equipment Co, LTD, China) and was weighed until reaching constant weight. All the measurements were repeated three times, the average values are reported. The mole fraction of TME in the corresponding solvent can be calculated by Eq. (1):

$$x_A = \frac{m_1/M_1}{m_1/M_1 + \sum_i^N m_i/M_i} \quad (1)$$

where x_A represents the mole fraction solubility of TME at different solvents, m_1 and M_1 are the mass and molar mass of the solute, m_i and M_i ($i = 2, \dots, N$) the mass and molar mass of solvent, respectively. When $N = 2$, it means the pure solvent, and $N = 3$ represents the binary solvent mixture.

2.5. Simulation methods

Density functional theory (DFT) calculations were carried out to disclose the reason that TME has different solubility in different individual solvent. All the calculations were performed with the Materials StudioDMol3 program from Accelrys [11]. A double numerical plus polarization (DNP) basis set has been used to describe the valence orbital of the O, C and H atoms.

The accuracy of the DNP basis set has been analyzed in detail by Delley. The nonlocal exchange and correlation energies were calculated with the Becke–Lee–Yang–Parr (BLYP) functional of the generalized gradient approximation (GGA) [12]. The convergence criteria consisted of threshold values of $1 \times 10^{-5} \text{ Eh}$ ($1 \text{ Eh} = 2625.5 \text{ kJ} \cdot \text{mol}^{-1}$), $0.02 \text{ Eh} \cdot \text{nm}^{-1}$, and 0.05 nm for energy, force, and displacement convergence, respectively, whereas a self-consistent-field (SCF) density convergence threshold value of $1 \times 10^{-6} \text{ Eh}$ ($1 \text{ Eh} = 2625.5 \text{ kJ} \cdot \text{mol}^{-1}$) was specified. A Fermi smearing of 0.005 Eh ($1 \text{ Eh} = 2625.5 \text{ kJ} \cdot \text{mol}^{-1}$) was used to improve computational performance, and the solvent effect was also considered during the calculations. The geometries of all stationary points were fully optimized at this level. The interaction energy was defined as

$$E_{\text{inter}} = E_{\text{TME-solvent}} - E_{\text{TME}} - E_{\text{solvent}} \quad (2)$$

where E_{TME} , E_{solvent} and $E_{\text{TME-solvent}}$ were the energy of TME, solvent, total energy of TME with solvent, respectively.

3. Results and Discussion

3.1. Thermal analysis

The melting point (T_m) and the molar enthalpy change (ΔH_{fus}) are important thermodynamic properties, and they are also necessary information for some models.

A TGA/DSC thermogram of TME is shown in Fig. 3. The first endothermic peak in Fig. 3 denotes that trimethylolethane undergoes a solid–solid phase transition, which is attributed to the breakage of some hydrogen bonds among the molecules [13]. The melting point (T_m) of

TME is 473.06 K, which can be determined by the second small endothermic peak. The values reported in previous literatures are in the range of (471.15 K to 476.15 K) [14–17]. So the result is in accordance with previous findings.

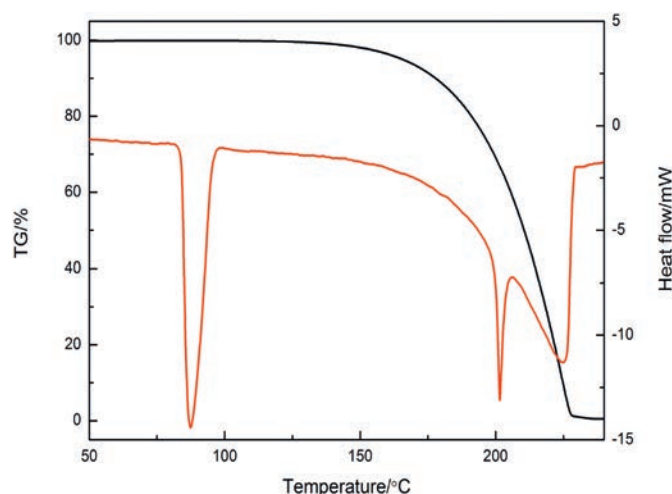


Fig. 3. Thermal analysis (DSC/TG) of TME.

Moreover, as is shown in Fig. 3, sublimation of TME began before it melted, which revealed that the determined fusion enthalpy of TME contained evaporation heat, and the conventional calorimetric test could not be used to measure the fusion enthalpy of TME. To circumvent this problem, a semi empirical equation was applied to estimate the fusion entropy of TME (ΔS_{fus}) [18]:

$$\Delta S_{fus} = C - R \ln \sigma + R \ln \phi \quad (3)$$

$$\phi = 2.85^{[SP3 + 0.5SP2 + 0.5RING - 1]} \quad (4)$$

where C is the entropy of melting constant, the average value of C is close to $50 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. σ and ϕ represent the molecular symmetry number and molecular flexibility number, respectively. $SP3$ is the number of sp^3 chain atoms, $SP2$ the number of sp^2 chain atoms, and $RING$ the number of fused-ring systems. R is the gas constant.

Then the fusion enthalpy can be calculated by the following equation:

$$\Delta H_{fus} = T_m \Delta S_{fus} \quad (5)$$

The estimated molar enthalpy of fusion (ΔH_{fus}) of TME is $29.83 \text{ kJ} \cdot \text{mol}^{-1}$. According to literature [19], the average error of the estimated values of ΔS_{fus} is $12.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

3.2. Solubility data

The solubility values of TME from 283.15 K to 328.15 K in the selected solvents are listed in Tables 1, 2, 3 and graphically plotted in Figs. 4–7.

It can be observed from Fig. 3, that the solubility of TME increases with the increase of temperature, and the order of the solubility of TME is butanol > methyl acetate > ethyl acetate at a given high temperature. The polarity order of these solvents is methyl acetate > ethyl acetate > butanol [20], and the results show that the solubility is high in the strong polar solvents. However, the solubility of TME does not increase along with the solvent polarity, and the solubility is relatively high in butanol than in esters, attributing to the easy formation of hydrogen bonds between TME and butanol molecules, which is confirmed by the molecular modeling results (Fig. 5 and Table 4). DFT calculations were performed to disclose the potential

Table 1

Experimental (x^{exp}) and calculated (x^{cal}) mole fraction solubility of TME in mono-solvents from 283.15 K to 318.15 K under 101 kPa

T/K	100x ^{exp}	100x ^{cal}		
		van't Hoff	Modified Apelblat	λh
Butanol				
283.15	3.859	3.713	3.832	3.703
288.15	4.485	4.511	4.525	4.522
293.15	5.353	5.445	5.365	5.476
298.15	6.341	6.531	6.383	6.580
303.15	7.691	7.786	7.618	7.844
311.05	9.139	9.230	9.119	9.282
313.15	11.00	10.88	10.94	10.90
318.15	13.08	12.76	13.16	12.71
Methyl acetate				
283.15	0.2604	0.2496	0.2580	0.2566
288.15	0.3172	0.3218	0.3211	0.3337
293.15	0.3980	0.4113	0.4013	0.4259
298.15	0.5118	0.5214	0.5036	0.5391
303.15	0.6376	0.6558	0.6341	0.6833
311.05	0.8011	0.8188	0.8009	0.8629
313.15	0.9970	1.015	1.014	1.068
318.15	1.300	1.250	1.228	1.312
Ethyl acetate				
283.15	0.2050	0.2035	0.2052	0.2173
288.15	0.2625	0.2629	0.2630	0.2811
293.15	0.3346	0.3367	0.3352	0.3571
298.15	0.4330	0.4277	0.4251	0.4501
303.15	0.5278	0.5390	0.5363	0.5680
311.05	0.6734	0.6743	0.6733	0.7143
313.15	0.8413	0.8376	0.8451	0.8806
318.15	1.050	1.034	1.047	1.079

Standard uncertainties u are $u(T) = 0.1 \text{ K}$, $u(x^{exp}) = 0.02$, $u(p) = 0.4 \text{ kPa}$.

interactions between TME and different solvent molecules, including methanol, ethanol, butanol and ethyl acetate. As is shown in Fig. 5 and Table 4, TME molecule interacts with methanol or ethanol to form hydrogen bonding between the oxygen atoms alcohol molecules and hydrogen atoms of TME, with the interaction energy of $-23.69 \text{ kJ} \cdot \text{mol}^{-1}$ and $-20.33 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. For the butanol, there appear two hydrogen bonds between TME and butanol, and the interaction energy is $-9.51 \text{ kJ} \cdot \text{mol}^{-1}$. In the case of the solvent methyl acetate, the atom O of methyl acetate can form hydrogen bond with atom H of TME with the interaction energy is $-1.59 \text{ kJ} \cdot \text{mol}^{-1}$. The larger the energy value of E_{inter} is, the stronger interactions occur between TME and the solvent molecules. It is the stronger hydrogen bonds between alcohols and TME that results in the higher solubility of TME in alcohols.

For the binary solvent mixtures, the solubility of TME also increases with the increasing temperature at the constant solvent composition. Besides, it also increases with the increasing of proportion of methanol or ethanol at a given temperature, as is shown in Tables 2 and 3.

3.3. Data correlation

3.3.1. In pure solvents

The quantitative relation between temperature and solubility of TME in each solvent can be correlated by the following thermodynamic models.

3.3.1.1. Van't Hoff equation. The relationship between the molar fraction solubility data and temperature for a real solution can be associated with the van't Hoff equation, which is formulated as follows:

$$\ln x = -\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R} \quad (6)$$

Table 2
Experimental and calculated mole fraction solubility of TME in methanol(x_a)-ethyl acetate binary solvents from 283.15 K to 318.15 K under 101 kPa

T/K	100 x^{exp}	100 x^{cal}			
		van'tHoff	Modified Apelblat	CNIBS/R-K	Modified Jouyban–Acree
0.1739					
283.15	0.9377	0.8945	0.9367	0.9377	0.8681
288.15	1.075	1.103	1.102	1.075	1.049
293.15	1.342	1.351	1.310	1.342	1.269
298.15	1.615	1.644	1.572	1.615	1.537
303.15	1.955	1.987	1.903	1.905	1.864
308.15	2.358	2.386	2.324	2.258	2.264
313.15	2.803	2.850	2.859	2.803	2.750
318.15	3.546	3.384	3.543	3.546	3.344
0.2849					
283.15	1.608	1.514	1.602	1.608	1.621
288.15	1.842	1.858	1.867	1.842	1.936
293.15	2.218	2.264	2.203	2.218	2.317
298.15	2.654	2.741	2.629	2.654	2.777
303.15	3.214	3.298	3.169	3.214	3.334
308.15	3.762	3.944	3.858	3.762	4.007
313.15	4.735	4.689	4.739	4.735	4.822
318.15	5.914	5.546	5.869	5.914	5.808
0.49486					
283.15	3.653	3.397	3.613	3.652	3.660
288.15	4.103	4.138	4.161	4.104	4.304
293.15	4.837	5.006	4.860	4.837	5.075
298.15	5.730	6.017	5.750	5.729	5.997
303.15	7.043	7.189	6.886	7.043	7.100
308.15	8.231	8.540	8.340	8.230	8.421
313.15	10.30	10.09	10.20	10.30	10.003
318.15	12.53	11.86	12.61	12.531	11.898
0.7133					
283.15	6.525	6.376	6.493	6.523	6.096
288.15	7.492	7.576	7.590	7.493	7.098
293.15	8.891	8.949	8.875	8.892	8.288
298.15	10.45	10.51	10.38	10.45	9.702
303.15	12.35	12.28	12.14	12.35	11.38
308.15	13.99	14.28	14.19	13.99	13.38
313.15	16.38	16.52	16.60	16.38	15.76
318.15	19.63	19.03	19.41	19.63	18.60
0.8523					
283.15	7.367	7.124	7.364	7.363	7.773
288.15	8.457	8.448	8.474	8.458	9.006
293.15	9.802	9.959	9.803	9.802	10.46
298.15	11.43	11.68	11.40	11.42	12.19
303.15	13.34	13.62	13.31	13.75	14.24
308.15	15.60	15.80	15.60	15.20	16.67
313.15	18.23	18.25	18.36	18.26	19.55
318.15	21.78	20.98	21.69	21.79	22.97

Standard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.05$ kPa, $u(x^{\text{exp}}) = 0.02$.

where ΔH_d and ΔS_d are the dissolution enthalpy and entropy respectively, and R is for gas constant. The above equation can be written as Eq. (6) when the dissolution enthalpy and entropy were considered to be independent of temperature in the lower temperature range [21]:

$$\ln x = A + \frac{B}{T/K} \tag{7}$$

where x is the molar fraction solubility of TME, T is the corresponding temperature, and A and B are constant parameters regressed with the linear solubility curve of $\ln x$ versus $1/T$.

3.3.1.2. Modified Apelblat Equation. The solubility data was correlated by the Modified Apelblat equation, a commonly used semi-empirical model as [22]:

$$\ln x = A + \frac{B}{T/K} + C \ln \frac{T}{K} \tag{8}$$

Table 3
Experimental and calculated mole fraction solubility of TME in ethanol(x_b)-ethyl acetate binary solvents from 283.15 K to 318.15 K under 101 kPa

T/K	100 x^{exp}	100 x^{cal}			
		van'tHoff	Modified Apelblat	CNIBS/R-K	Modified Jouyban–Acree
0.1025					
283.15	0.5205	0.4909	0.5044	0.5205	0.5007
288.15	0.609	0.624	0.626	0.609	0.622
293.15	0.751	0.787	0.777	0.751	0.773
298.15	0.981	0.985	0.966	0.980	0.961
303.15	1.217	1.224	1.201	1.217	1.192
308.15	1.496	1.509	1.494	1.496	1.479
313.15	1.887	1.849	1.859	1.887	1.834
318.15	2.280	2.251	2.313	2.280	2.271
0.2968					
283.15	1.532	1.453	1.511	1.533	1.493
288.15	1.781	1.794	1.800	1.781	1.809
293.15	2.103	2.198	2.157	2.103	2.194
298.15	2.631	2.675	2.599	2.631	2.662
303.15	3.215	3.235	3.148	3.215	3.232
308.15	3.794	3.887	3.831	3.794	3.927
313.15	4.720	4.644	4.683	4.720	4.771
318.15	5.705	5.517	5.747	5.705	5.798
0.4950					
283.15	3.061	2.893	3.034	3.061	2.953
288.15	3.497	3.529	3.544	3.497	3.512
293.15	4.161	4.275	4.178	4.161	4.185
298.15	5.031	5.146	4.968	5.031	4.995
303.15	5.972	6.156	5.954	5.971	5.971
308.15	7.051	7.323	7.188	7.052	7.146
313.15	8.958	8.662	8.737	8.957	8.562
318.15	10.58	10.19	10.69	10.58	10.27
0.6979					
283.15	4.705	4.464	4.683	4.705	4.714
288.15	5.405	5.385	5.409	5.405	5.522
293.15	6.264	6.455	6.308	6.264	6.487
298.15	7.317	7.691	7.423	7.317	7.640
303.15	9.047	9.111	8.809	9.045	9.019
308.15	10.45	10.73	10.54	10.45	10.67
313.15	12.77	12.58	12.69	12.77	12.65
318.15	15.31	14.67	15.39	15.31	15.01
0.8976					
283.15	6.119	5.937	6.119	6.119	6.291
288.15	7.196	7.128	7.148	7.196	7.283
293.15	8.347	8.505	8.382	8.346	8.462
298.15	9.708	10.09	9.864	9.707	9.86
303.15	11.82	11.90	11.65	11.81	11.53
308.15	13.73	13.96	13.79	13.73	13.52
313.15	16.61	16.29	16.38	16.61	15.90
318.15	19.33	18.92	19.50	19.33	18.73

Standard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.05$ kPa, $u(x^{\text{exp}}) = 0.02$.

where T is the absolute temperature, and A , B and C are the model parameters fitted by the experimental solubility data.

3.3.1.3. λh Equation. The λh equation was initially proposed by Buchowski to reflect the solubility behavior of the solute in solution. It's also a semi-empirical equation as [23]:

$$\ln \left[1 + \lambda \left(\frac{1-x}{x} \right) \right] = \lambda h \left(\frac{1}{T} - \frac{1}{T_m} \right) \tag{9}$$

where T_m is the melting temperature of Kelvin, and λ (representing the no ideality of solution system) and h (representing the enthalpy of solution) are the two adjustable parameters given from the solubility data.

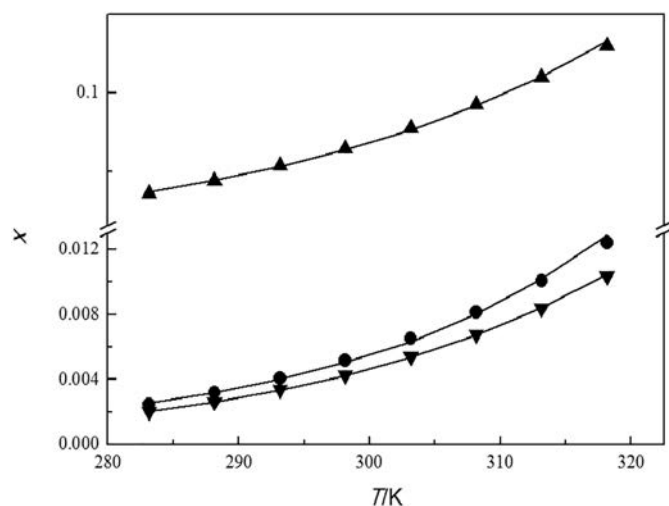


Fig. 4. Experimental and correlated mole fraction solubility of TME in mono-solvents: ▲, butanol; ●, methyl acetate; ▼, ethyl acetate. The solid lines are fitted curves with the modified Apelblat equation.

3.3.2. In binary solvent mixtures

The quantitative relation between temperature and solubility of TME in binary solvent mixtures can be correlated by the following thermodynamic models.

3.3.2.1. CNIBS/R-K Model. The CNIBS/R-K model is defined as [24]:

$$\ln x = x_A^0 \ln x_A + x_B^0 \ln x_B + x_A^0 x_B^0 \sum_{i=0}^2 S_i (x_A^0 - x_B^0)^i \quad (10)$$

where x is the mole fraction solubility of the solute, x_A^0 and x_B^0 are the initial mole fraction of methanol and ethyl acetate, and x_A and x_B represent the mole fraction solubility of the solute in pure solvents, respectively. S_i is the model constant.

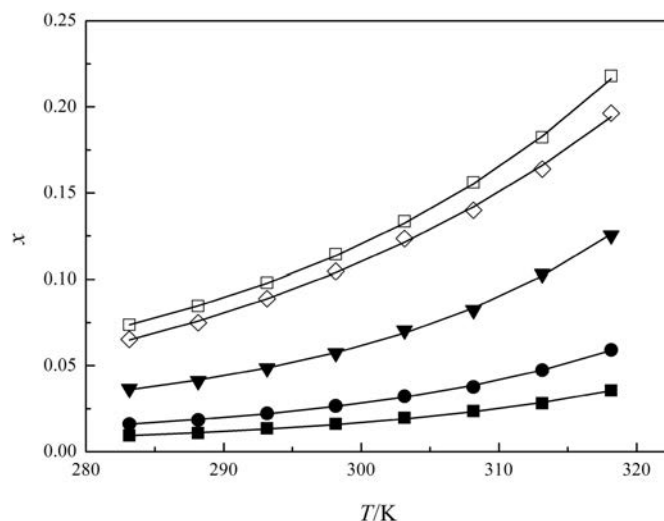


Fig. 6. Mole fraction solubility of TME in binary solvents methanol-ethyl acetate at different molar fraction of methanol (x_a): ■, $x_a = 0.1739$; ●, $x_a = 0.2849$; ▼, $x_a = 0.4949$; ◇, $x_a = 0.7133$; □, $x_a = 0.8524$. —, calculated by the modified Apelblat equation.

x_B^0 can be replaced by $(1 - x_A^0)$, then Eq. (10) can be simplified as following:

$$\ln x = B_0 + B_1 x_A^0 + B_2 (x_A^0)^2 + B_3 (x_A^0)^3 + B_4 (x_A^0)^4 \quad (11)$$

where B_0 , B_1 , B_2 , B_3 and B_4 are the model parameters which could be obtained by least-squares regression.

3.3.2.2. Jouyban–Acree Model. This is a versatile model to describe the effect of both temperature and solvent composition on the solubility data, the model for representing the solubility of a solute in a binary mixtures [25]:

$$\ln x = x_A \ln X_A + x_B \ln X_B + x_A x_B \sum_{i=0}^N \frac{J_i (x_A - x_B)^i}{T} \quad (12)$$

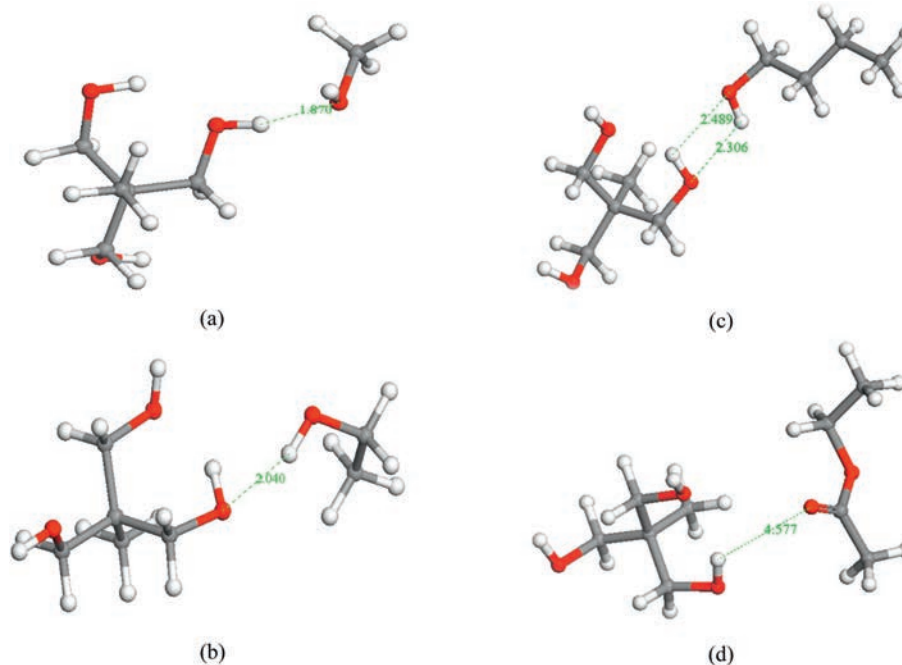


Fig. 5. Interactions between TME and methanol (a), ethanol (b), butanol (c), ethyl acetate (d), respectively.

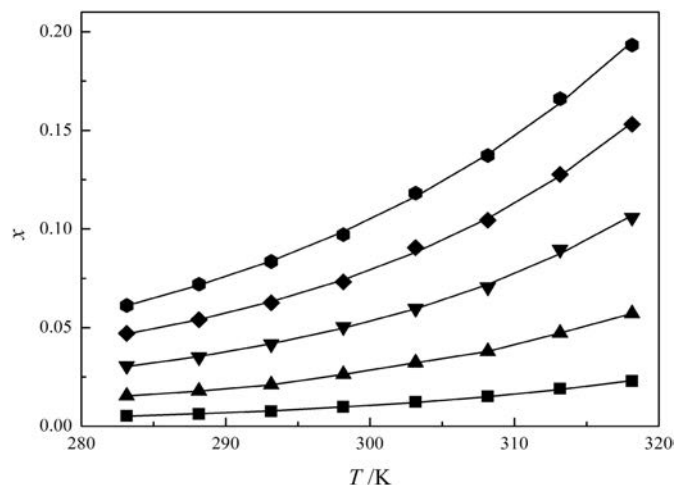


Fig. 7. Experimental and correlated mole fraction solubility of TME in binary solvents ethanol-ethyl acetate at different molar fraction of ethanol (x_B): ■, $x_B = 0.1025$; ▲, $x_B = 0.2968$; ▼, $x_B = 0.4950$; ◆, $x_B = 0.6979$; ●, $x_B = 0.8976$. —, calculated by the modified Apelblat equation.

Table 4

The sum of interaction energy between TME and solvent molecules

	Methanol	Ethanol	Butanol	Ethyl acetate
$E_{\text{inter}}/\text{kJ} \cdot \text{mol}^{-1}$	−23.69	−20.33	−9.51	−1.59

Table 5

λh correlation parameters of TME in mono-solvents

Solvent	λ	h	100RAD	100RMSD
Butanol	4.51	746.30	2.28	0.19
Ethyl acetate	0.76	5509.89	0.82	0.01
Methyl acetate	0.89	4662.21	2.69	0.02

Average (100RAD) = 1.93

where J_i is a model constant, and x_A and x_B represent the initial mole fraction composition of the binary solvents when the solute was not added. The X_A and X_B represent the saturated mole solubility of

TME in methanol and ethyl acetate respectively. When $N = 2$ and substituting $(1 - x_A)$ for x_B in Eq. (12), subsequent rearrangements result in Eq. (13).

$$\ln x = x_A \ln X_A + (1 - x_A) \ln X_B + \frac{(J_0 - J_1 + J_2)x_A}{T} + \frac{(-J_0 + 3J_1 - 5J_2)x_A^2}{T} + \frac{(-2J_1 + 8J_2)x_A^3}{T} + \frac{(-4J_2)x_A^4}{T} \quad (13)$$

Substituting the modified Apelblat equation into Eq. (13), equation can be expressed as follows:

$$\ln x = x_A \left(A_1 + \frac{B_1}{T} + C_1 \ln T \right) + (1 - x_A) \left(A_2 + \frac{B_2}{T} + C_2 \ln T \right) + \frac{(J_0 - J_1 + J_2)x_A}{T} + \frac{(-J_0 + 3J_1 - 5J_2)x_A^2}{T} + \frac{(-2J_1 + 8J_2)x_A^3}{T} + \frac{(-4J_2)x_A^4}{T} \quad (14)$$

Eq. (14) can be further simplified as follows after introducing a constant term:

$$\ln x = A_0 + \frac{A_1}{T} + A_2 \ln T + A_3 x_A + \frac{A_4 x_A + A_5 x_A^2 + A_6 x_A^3 + A_7 x_A^4}{T} + A_8 x_A \ln T \quad (15)$$

where $A_0, A_1, A_2, A_3, A_4, A_5, A_6, A_7$, and A_8 are parameters of this model.

All the parameters of above models are shown in Tables 5–8.

The average relative deviation (RAD), and the root-mean-square deviations (RMSD) are defined as in the following formula to evaluate the accuracy of the model [26].

$$\text{RAD} = \frac{1}{N} \sum_{i=1}^N \left| \frac{x_{1,i} - x_{1,i}^{\text{cal}}}{x_{1,i}} \right| \quad (16)$$

$$\text{RMSD} = \left[\frac{\sum_{i=1}^N (x_{1,i}^{\text{cal}} - x_{1,i})^2}{N} \right]^{1/2} \quad (17)$$

Table 6

van't Hoff and Modified Apelblat correlation parameters in mono-solvents and binary solvents

	van't Hoff				Modified Apelblat				
	A	B	100RAD	100RMSD	A	B	C	100RAD	100RMSD
Butanol	7.93	−3178.24	1.85	0.16	−165.72	4512.70	25.95	0.61	0.05
Ethyl acetate	8.62	−4196.38	0.86	0.01	−59.79	−1133.49	10.20	0.56	0.01
Methyl acetate	8.61	−4136.53	2.35	0.02	−257.19	7753.99	39.65	0.98	0.01
	Average (100RAD) = 1.68				Average (100RAD) = 0.72				
Methanol- ethyl acetate									
x_b	A	B	100RAD	100RMSD	A	B	C	100RAD	100RMSD
0.1739	−3424.90	7.38	2.34	0.07	−233.91	7370.69	35.99	1.73	0.04
0.2849	−3341.74	7.61	3.34	0.16	−386.38	14286.68	58.77	1.02	0.04
0.4949	−3216.888	7.98	3.71	0.32	−418.63	15870.81	63.63	1.06	0.09
0.7133	−2819.61	7.21	1.40	0.25	−119.91	2867.81	18.96	1.04	0.16
0.8524	−2780.38	7.18	1.80	0.34	−221.64	7457.31	34.13	0.24	0.06
	Average (100RAD) = 2.72				Average (100RAD) = 1.07				
Ethanol- ethyl acetate									
x_b	A	B	100RAD	100RMSD	A	B	C	100RAD	100RMSD
0.1025	−3919.47	8.53	2.30	0.03	−200.89	5447.55	31.24	1.91	0.02
0.2968	−3433.15	7.89	2.51	0.09	−267.10	8866.55	41.02	1.35	0.04
0.4950	−3241.03	7.90	3.17	0.22	−322.19	11529.06	49.24	1.20	0.10
0.6979	−3062.14	7.70	2.84	0.31	−325.61	11851.19	49.72	0.91	0.11
0.8976	−2983.64	7.71	2.01	0.26	−202.27	6411.65	31.32	0.86	0.13
	Average (100RAD) = 2.57				Average (100RAD) = 1.25				

Table 7

CNIBS/R-K model correlation parameters in methanol-ethyl acetate and ethanol-ethyl acetate binary solvents

Methanol-ethyl acetate							
T/K	B ₀	B ₁	B ₂	B ₃	B ₄	100RAD	100RMSD
283.15	−5.78	7.60	−8.31	8.74	−5.07	0.49	0.02
288.15	−5.75	8.89	−13.48	16.53	−8.98	0.40	0.02
293.15	−5.43	8.26	−13.20	17.92	−10.29	0.24	0.01
298.15	−5.26	8.37	−13.54	18.19	−10.36	0.54	0.03
303.15	−6.55	11.72	−10.28	7.95	−5.81	0.46	0.03
308.15	−4.21	6.56	−6.47	6.78	−4.86	0.38	0.03
313.15	−4.49	5.55	−1.12	−2.59	0.90	0.38	0.04
318.15	1.10	−2.26	−1.98	5.90	−4.27	0.51	0.06
Average (100RAD) = 0.43							
Ethanol-ethyl acetate							
T/K	B ₀	B ₁	B ₂	B ₃	B ₄	10 ⁴ RAD	10 ⁴ RMSD
283.15	−6.04	8.51	−8.76	4.48	−0.88	0.17	0.01
288.15	−5.91	8.87	−10.40	6.80	−1.89	0.21	0.01
293.15	−5.58	7.30	−4.83	−1.15	1.96	0.09	0.01
298.15	−5.28	6.79	−3.61	−3.02	3.00	0.25	0.01
303.15	−5.15	8.14	−10.02	7.45	−2.47	1.55	0.20
308.15	−4.85	6.85	−5.60	1.15	0.61	0.41	0.05
313.15	−4.51	5.31	0.73	−8.50	5.41	0.60	0.06
318.15	−4.39	6.41	−4.07	−0.10	1.53	0.27	0.04

Average (10⁴RAD) = 0.44**Table 8**

Modified Jouyban–Acree model correlation parameters in methanol-ethyl acetate and ethanol-ethyl acetate binary solvents

Parameters	Methanol-ethyl acetate	Ethanol-ethyl acetate
A ₀	−173.20	−145.69
A ₁	4221.67	2721.03
A ₂	26.96	23.01
A ₃	−0.67	−48.23
A ₄	2683.05	5271.61
A ₅	−2488.83	−3758.17
A ₆	992.20	3215.82
A ₇	−7.34	−1207.93
A ₈	0.05	6.95
100RAD	3.93	2.04
100RMSD	0.46	0.21

where N represents the number of experimental points, and x_1 and x_1^{cal} stand for the values of solubility measured and calculated, respectively.

The results show that the Modified Apelblat Equation gives the best fitting results of the solubility data of TME in the pure solvents, while the CNIBS/R-K model fits the solubility data of TME in the binary solvent mixtures well.

3.4. Thermodynamic properties of the dissolution process.

According to the thermodynamic principles, the thermodynamic properties of the molar enthalpy (ΔH_d) and the molar entropy (ΔS_d) of the dissolution process were calculated from the van't Hoff equation [27].

The $\ln x$ vs $1/T$ plots are shown in Figs. 8, 9 and 10. We can observe that the solubility data has a linear relationship with the reciprocal of temperature. The molar enthalpy (ΔH_d) and the molar entropy (ΔS_d) were determined from the slope and intercept of $\ln x$ vs $1/T$.

The thermodynamic properties estimated by above-mentioned equation are given in Table 9. It can be seen that the dissolving process of TME in all solvents are endothermic since ΔH_d of the dissolution process is positive, which declares the solubility of TME increases with

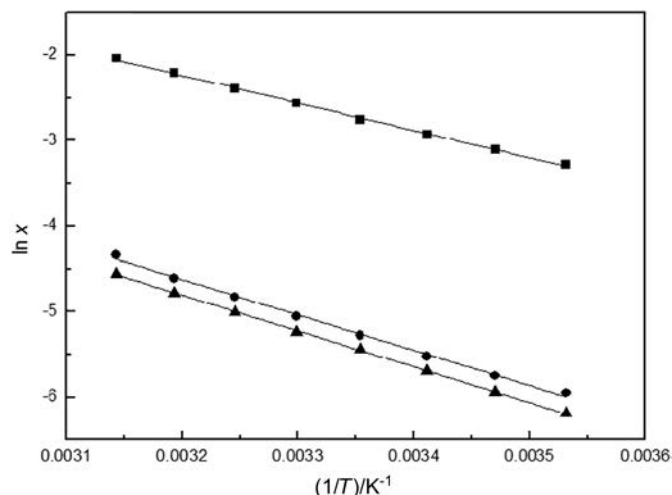


Fig. 8. The van't Hoff plot of logarithm molar fraction solubility ($\ln x$) of TME vs $(1/T)$ in three pure solvents. (■) butanol; (●) methyl acetate; (▲) ethyl acetate.

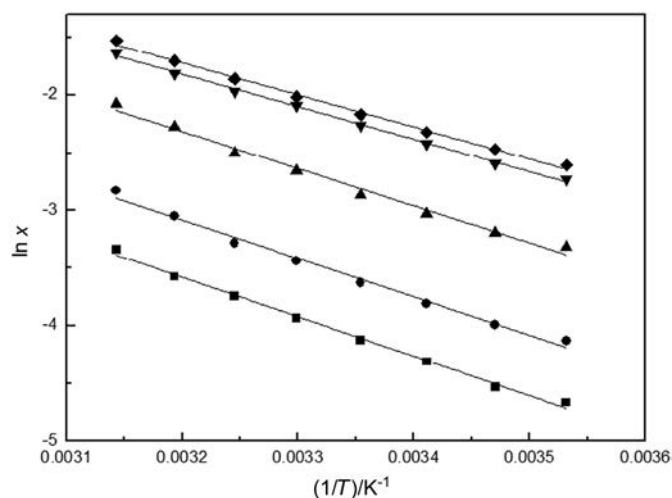


Fig. 9. The van't Hoff plot of logarithm molar fraction solubility ($\ln x$) of TME vs $(1/T)$ in binary solvents methanol-ethyl acetate at different molar fraction of methanol (x_a). ♦, $x_a = 0.1739$; ▼, $x_a = 0.2849$; ▲, $x_a = 0.4949$; ●, $x_a = 0.7133$; ■, $x_a = 0.8524$.

increasing temperature. These results are very useful for optimizing the dissolution and crystallization of TME.

4. Conclusions

The solubility of TME in selected organic solvents is determined by the gravimetric method under atmosphere pressure and the temperature ranging from 283.15 K to 318.15 K. The experiment values are correlated by Van't Hoff equation, Modified Apelblat Equation, λh Equation, CNIBS/R-K Equation, and Jouyban–Acree Model. The Modified Apelblat Equation gives the best fitting results of the solubility data of TME in the pure solvents while the CNIBS/R-K model fits the solubility data of TME in the binary solvent mixtures well. The thermodynamic properties of the dissolution process are calculated and the results show that the dissolution process is endothermic. The experiment values in this study can be used for the purification process of TME in industry.

Nomenclature

A, B, C semi empirical constants
A₀–A₈ semi empirical constants
B₀–B₄ semi empirical constants

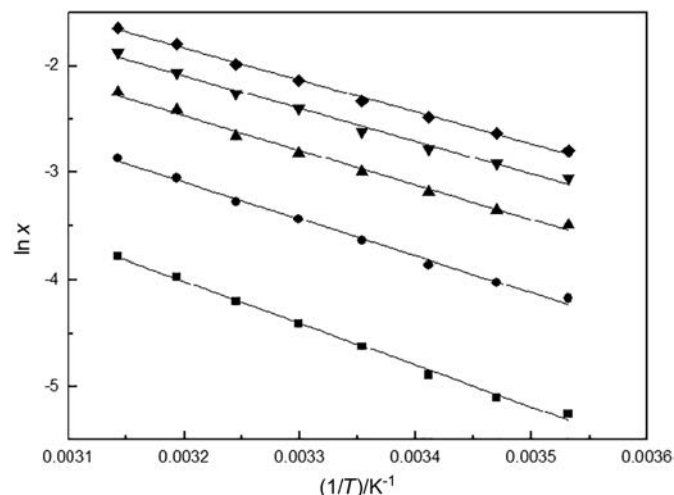


Fig. 10. The van't Hoff plot of logarithm molar fraction solubility ($\ln x$) of TME vs $(1/T)$ in binary solvents ethanol-ethyl acetate at different molar fraction of ethanol (x_b). $\blacklozenge$, $x_b = 0.1025$; $\blacktriangledown$, $x_b = 0.2968$; $\blacktriangle$, $x_b = 0.4950$; $\bullet$, $x_b = 0.6979$; $\blacksquare$, $x_b = 0.8976$.

Table 9

Standard dissolution enthalpy of TME in individual liquid and methanol-ethyl acetate, ethanol-ethyl acetate binary solvents the temperature ranging from $T = 283.15$ K to 318.15 K under 101 kPa

Solvent	$\Delta H_d/\text{J} \cdot \text{mol}^{-1}$	$\Delta S_d/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	R^2
Butanol	26,420.06	67.19	0.9974
Methyl acetate	34,388.95	71.59	0.9972
Ethyl acetate	34,885.07	71.67	0.9984
<i>Methanol (x_a)-ethyl acetate</i>			
0.1739	28,478.53	61.36	0.9953
0.2849	27,784.47	63.29	0.9901
0.3929	26,738.99	66.32	0.9878
0.4949	23,439.24	59.89	0.9975
0.7133	23,113.00	59.67	0.9956
0.8524	28,478.53	61.36	0.9953
<i>Ethanol(x_b)-ethyl acetate</i>			
0.1025	32,577.00	70.85	0.9959
0.2968	28,583.78	65.77	0.9946
0.4950	26,949.75	65.72	0.9919
0.6979	25,463.29	64.08	0.9914
0.8976	24,807.56	64.13	0.9960

E_{TME}	the energy of TME
$E_{\text{TME-solvent}}$	the total energy of TME with solvent
E_{solvent}	the energy of solvent
h	enthalpy of solution, $\text{kJ} \cdot \text{mol}^{-1}$
M_1, M_2, M_3	molecular weights of solute, methanol and ethyl acetate, respectively, $\text{g} \cdot \text{mol}^{-1}$
m_0, m_1, m_1	mass of solute, methanol and ethyl acetate, respectively, g
n	number of experimental data points
R	gas constant, $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
RAD	average relative deviation
RMSD	root-mean-square deviations
T	absolute temperature, K
T_m	melting point, K
x_A	mole fraction of solute
x^{exp}	experimental values
ΔH_{fus}	enthalpy of fusion, $\text{kJ} \cdot \text{mol}^{-1}$
ΔS_{fus}	entropy of fusion, $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
ΔH_d	dissolution enthalpy, $\text{kJ} \cdot \text{mol}^{-1}$
λ	no ideality of solution system

References

- [1] J.S. Pan, W.B. Jia, X.Q. Zhang, *et al.*, Synthesis technology of trimethylolethane, *Appl. Chem. Ind.* 38 (2009) 465–468.
- [2] H. Suzuki, N. Wada, Y. Komoda, H. Usui, S. Ujiie, Drag reduction characteristics of trimethylolethane hydrate slurries treated with surfactants, *Int. J. Refrig.* 32 (2009) 931–937.
- [3] W. Wu, Y.F. Chen, X. Shi, S.C. Zhang, H.R. Sun, Preparation and properties of polyalcohol phase change material for insulation, *Key Eng. Mater.* 512–515 (2012) 936–939.
- [4] M.O. Robeson, Continuous production of trimethylolethane, US Pat., 2790837(1957).
- [5] P.E. Eckler, Crystallization-inhibited trimethylolethane solutions, US Pat., 4709104(1987).
- [6] S.D.A. Lorenzo, Recovering trimethylolethane by ethyl acetate extraction, US Pat., 2806892(1957).
- [7] X.Z. Shao, W.W. Chen, W. Liu, H.T. Yun, Measurement and correlation of trimethylolethane solubility in different solvents, *J. Chem. Eng. Chin. Univ.* 30 (2016) 967–970 (in Chinese).
- [8] N.N. Tian, L.S. Wang, M.Y. Li, Y. Li, R.Y. Jiang, Solubilities of phenylphosphinic acid, methylphenylphosphinic acid, hexachlorocyclotriphosphazene, and hexaphenoxycyclotriphosphazene in selected solvents, *J. Chem. Eng. Data* 56 (2011) 661–670.
- [9] D. Mealey, M. Svärd, Å.C. Rasmuson, Thermodynamics of risperidone and solubility in pure organic solvents, *Fluid Phase Equilib.* 375 (2014) 73–79.
- [10] H. Wu, L. Dang, H. Wei, Solid-liquid phase equilibrium of nicotinamide in different pure solvents: measurements and thermodynamic modeling, *Ind. Eng. Chem. Res.* 53 (2014) 1707–1711.
- [11] B. Delley, An all-electron numerical method for solving the local density functional for polyatomic molecules, *J. Chem. Phys.* 92 (1990) 508–517.
- [12] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B Condens. Matter* 37 (1988) 785–789.
- [13] K. Suenaga, T. Matsuo, H. Suga, Heat capacity and phase transition of trimethylolethane, *Thermochim. Acta* 163 (1990) 263–270.
- [14] W.E. Doering, The acidity of bridgehead α -hydrogen in a bicyclic trisulfone, *J. Am. Chem. Soc.* 77 (1955) 509–513.
- [15] S. Olsen, A relationship between the tollens reaction and the formaldehyde-olefin reaction. The reaction of formaldehyde with propionaldehyde and cyclohexanone, *Acta Chem. Scand.* 7 (1953) 1364–1369.
- [16] R. Colson, Nitropentaglycerin eventual substitute for nitroglycerin continuous preparation and properties, *Mem. Poudres* 30 (1948) 43–58.
- [17] N.S. Marans, Nitrate esters of 2, 2-dimethylol-1-propanol monoacetate and diacetate, *J. Am. Chem. Soc.* 76 (1954) 3223–3224.
- [18] J. Akash, S.H. Yalkowsky, Estimation of melting points of organic compounds-II, *Ind. Eng. Chem. Res.* 95 (2006) 2562–2618.
- [19] R.M. Dannenfelser, S.H. Yalkowsky, Estimation of entropy of melting from molecular structure: A non-group contribution method, *Ind. Eng. Chem. Res.* 35 (1996) 1483–1486.
- [20] W. Yang, S. Fan, Q. Guo, J. Hao, H. Li, S. Yang, W. Zhao, J. Zhang, Y. Hu, Thermodynamic models for determination of the solubility of 4-(4-aminophenyl)-3-morpholinone in different pure solvents and (1,4-dioxane + ethyl acetate) binary mixtures with temperatures from (278.15 to 333.15) K, *J. Chem. Thermodyn.* 97 (2016) 214–220.
- [21] J.P. Fan, X.K. Xu, G.L. Shen, X.H. Zhang, Measurement and correlation of the solubility of genistin in eleven organic solvents from $T = (283.2 \text{ to } 323.2)$ K, *J. Chem. Thermodyn.* 89 (2015) 142–147.
- [22] W.G. Yang, S.M. Fan, Q.R. Guo, J.F. Hao, H.J. Li, S.H. Yang, W.D. Zhao, J. Zhang, Y.H. Hu, Thermodynamic models for determination of the solubility of 4-(4-aminophenyl)-3-morpholinone in different pure solvents and (1,4-dioxane + ethyl acetate) binary mixtures with temperatures from (278.15 to 333.15) K, *J. Chem. Thermodyn.* 97 (2016) 214–220.
- [23] S. Wang, Y.Y. Zhang, J.D. Wang, Solubility measurement and modeling for betaine in different pure solvents, *J. Chem. Eng. Data* 59 (2014) 2511–2516.
- [24] T.T. Wei, C. Wang, S.C. Du, S.G. Wu, J.Y. Li, J.B. Gong, Measurement and correlation of the solubility of penicillin v potassium in ethanol plus water and 1-butyl alcohol plus water systems, *J. Chem. Eng. Data* 60 (2015) 112–117.
- [25] J.P. Fan, B. Zheng, D.D. Liao, J.X. Yu, Y.H. Cao, X.H. Zhang, J.H. Zhu, Determination and modeling of the solubility of (limonin in methanol or acetone + water) binary solvent mixtures at $T = 283.2$ K to 318.2 K, *J. Chem. Thermodyn.* 98 (2016) 353–360.
- [26] C. Guo, L. Li, J. Cheng, J. Zhang, W. Li, Solubility of caprolactam in different organic solvents, *Fluid Phase Equilib.* 319 (2012) 9–15.
- [27] S.D. Zheng, Y. Han, J.L. Zhang, *et al.*, Determination and correlation of solubility of linezolid form II in different pure and binary solvents[J], *Fluid Phase Equilib.* 432 (2017) 18–27.