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Determination and correlation of solubility and solution thermodynamics of 1, 2-diphenylethane in different pure solvents

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The correlation of solubility and solution thermodynamics of 1,2- diphenylethane in different pure solvents has been studied. The mole fraction solubilities of 1, 2-diphenylethane in acetone, chloroform, dichloromethane, and ethanol increase with temperature**.** The mole fraction solubility in acetone, chloroform and dichloromethaneare much higher than that in ethanol and the mole fraction solubilities in chloroform and dichloromethane are higher than that in acetone. The solubility data were well correlated by the modified Apelblat,the semi-empirical Buchowski-Ksiazczak λh equation, and the ideal solution equation.The enthalpy, entropy and apparent free Gibbs energy of solution in different solvents were calculated. The dissolving process of 1,2-diphenylethane was endothermic, entropy-driving and not spontaneous.

Keywords: 1, 2-Diphenylethane, Correlation, Solubility, Thermodynamics

Boiling Point 284^{o}C; CAS Registry No.103-29-7; 1, 2-diphenylethane is famous as an aromaticchemical compound that can be considered a derivative of ethane in which one phenyl group connects each carbon atom, respectively. As its particular molecular structure, 1,2-diphenylethane has caused extensive concern in modern organic synthesis field. It is prone to participate in substitution, dehydrogenation, oxidation, and sulfonation reactions. As a significant intermediate, 1,2-diphenylethane is used in synthesizing flame retardant named 1,2-Bis(pentabromophenyl) ethane , leather tanning agent, fluorescent brightening agents, and dyestuff in chemical industry. In addition, it can form the central core of some stilbenoidnatural products and isoquinolinealkaloids, etc in medicine industry[1,2]. In industry, after 1,2-diphenylethane synthesis, the purity of raw product is often below 98.5%. However, it is badly in need of high purified 1,2-diphenylethanein drug synthesis field. In order to realize high purified 1,2-Diphenylethane , the traditional final treatment of raw 1,2-diphenylethaneis vacuum distillation. Although, the purity of 1,2-diphenylethane can not excess 99.5% through distillation under general situation. As all know, distillation consumes quite energy, and acquiring 99.5% purity of product also needs quite number of plates for distillation. Aiming at reaching high product purity, saving energy, and realizing industrial application, solution crystallization is introduced to purify 1,2-diphenylethane. In solution crystallization, the equilibrium data, especially solubility is an important property. Therefore, the solubilities of 1,2-diphenylethane in different pure solvents are absolutely necessary. However, the solubility data are few reported in the literature around the world. In the present work, the experimental solubility data inacetone,chloroform, dichloromethane, and ethanol were measured by static equilibrium method[3] from 278.15K to 298.15 K (or from 286.15K to 298.15 K) under the atmospheric pressure. The experimental values were correlated with the modified Apelblat equation, the semi-empirical Buchowski-Ksiazczak λh equation, and the ideal solution equation. The thermodynamic properties, including the Gibbs energy, entropy, enthalpy were also calculated.

Experimental Section

Materials

1,2-diphenylethane is purchased by Aladdin Industrial Corporation. It was prepared by recrystallization from acetone twice and then was washed with ethanol, dried in a vacuum drying oven at 303.15K for 24 hours and stored in a desiccator. Its mass fraction determined by GC-MS is better than 99.9%. Other reagentsare acetone**,** chloroform, dichloromethane, and ethanol from Sinopharm Chemical Reagent Co., Ltd.. The purities and sources of all materials were listed in Table 1.

Apparatus and Procedures

The measuring apparatus of the solubility is shown in Fig.1. A 100 mL sealed jacketed vessel was applied to determine the solubility of 1,2-Diphenylethane**.** Between the outer and inner walls of the vessel was filled with circulation coolant from a low thermostatic bath**.** The temperature was controlled by a low temperature thermostatic bath and its fluctuation is within 0.01°C. In the inner container, the solution was stirred by a magnetic stir bar and a alcohol thermometer (uncertainty of ± 0.05K) was also inserted in the liquid in order to read temperature. To prevent evaporationofthesolvent, a condenser was inserted in the hole on the top of the vessel**.** The masses of 1,2-Diphenylethane and solvents wered etermined by an analytical balance with anuncertainty of ± 0.1mg.

Before the experiment, when all the devices were set, a certain amount of solvent was added into the inner of the jacketed vessel and then the low temperature thermostatic bath was started. When the temperature reached the set point, the experiment could be carried out. The weighed excessive 1,2-Diphenylethane was added into the solvent and had been stirring for 12 hours at the fixed temperature. After attainingequilibrium, the stirrer was turned off tolet the solution settle for 3hours. Then the upper saturated solutions were drained by the dropper, filtered by the sintered-glass filter rapidly, and diverted into the ampoule immediately. Finally, the 1, 2-diphenylethane saturated solutions in the ampoule was diluted with solvent and absorbed by sampling probe for mass fraction analysis, using GC-MS. The mean value of mass fraction was taken from five measurements for each temperature. The mean values are used to calculate the mole fraction solubility (x_1)expressed as follow[4-8].

$$x_1 = \frac{w_1/M_1}{w_1/M_1 + w_2/M_2} \qquad \ldots(1)$$

Where w_1 and w_2 are the mass fraction of 1,2-diphenylethane and solvent respectively, M_1 and M_2 are the molecular weight of 1,2-diphenylethane and solvent respectively.

Results and Discussion

Solubility data

The measured experimental mole fraction solubility x_1 of 1,2-diphenylethane in acetone**,** chloroform, dichloromethane, and ethanolover the temperature range from 278.15K to 298.15K (orfrom 286.15K to 298.15K) under atmospheric pressure were listed in Table 2 and more visually presented in Fig. 2-4. From Table 2, it can be found that the mole fraction solubilityof 1,2-diphenylethane in all the tested solvents increased with temperature and the mole fraction solubility in acetone, chloroform and dichloromethaneare much higher than that in ethanol at the same temperature.In the view of mole fraction solubility, the ethanol is not suitable for using in solvent crystallization of 1,2-diphenylethane. Hence, the mole fraction solubility inacetone, chloroform and dichloromethane are focused on. The mole fraction solubility in chloroform and dichloromethane are higher than that in acetone at the temperature ranging from 278.15K to 298.15K. Within the temperature ranging from 278.15K to 283.15K, the mole fraction solubility

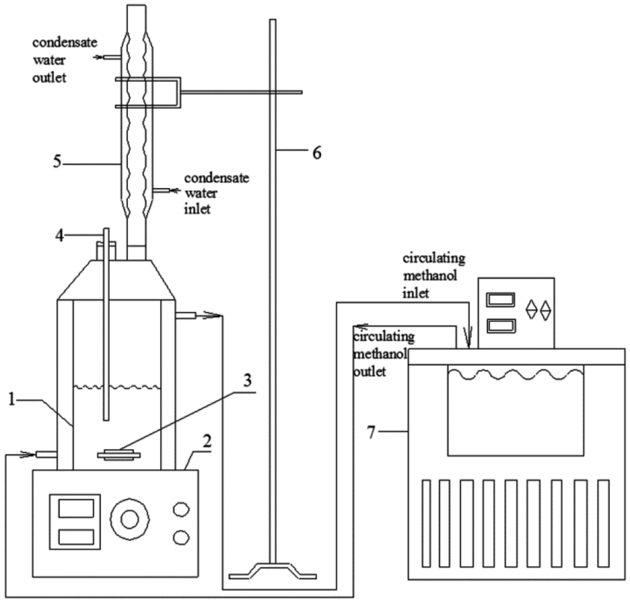

Fig.1 — Schematic diagram of determining solubility of 1,2-diphenylethane 1.jacketed vessel, 2.magnetic stirrer, 3.stir bar, 4.thermometer, 5.condenser, 6.iron support, 7.low temperature thermostatic bath

Table 1 — Details of the reagents used in the paper

Chemical name	CAS RN	Formula	MW	Mass fraction purity	Source
1,2-Diphenylethane	103-29-7	$C_{14}H_{14}$	182.26	≥99.9%	Aladdin Industrial Corporation
Chloroform	67-66-3	$CHCl_3$	119.38	≥99.5%	Sinopharm Chemical Reagent Co., Ltd.
Acetone	67-64-1	CH_3COCH_3	58.08	≥99.5%	
Dichloromethane	75-09-2	CH_2Cl_2	84.93	≥99.5%	
Ethanol	64-17-5	CH_3CH_2OH	46.07	≥99.7%	

Table 2 — Mole fraction solubility(x_1) of 1,2-diphenylethane in different pure solvents

T/K	x_1^a	x_1^{cal}		
		Apelblat equation	λ*h* equation	Ideal solution equation
Acetone				
278.15	0.2384	0.2371	0.2448	0.2237
283.15	0.2796	0.2628	0.2843	0.2864
288.15	0.3296	0.3098	0.3296	0.3634
293.15	0.4584	0.3867	0.3818	0.4575
298.15	0.6036	0.5092	0.4420	0.5715
Chloroform				
278.15	0.3744	0.3627	0.3037	0.3715
283.15	0.4331	0.4196	0.3864	0.4304
288.15	0.4758	0.4768	0.4758	0.4961
293.15	0.5879	0.5326	0.5677	0.5690
298.15	0.6465	0.5857	0.6576	0.6497
Dichloromethane				
278.15	0.3902	0.3587	0.4361	0.3893
283.15	0.4496	0.4133	0.4824	0.4384
288.15	0.4846	0.4887	0.5318	0.4916
293.15	0.5170	0.5919	0.5844	0.5491
298.15	0.6402	0.7330	0.6402	0.6111
Ethanol				
286.15	0.0266	0.0038	0.0266	0.0277
287.15	0.0282	0.0064	0.0279	0.0288
288.15	0.0302	0.0101	0.0293	0.0299
289.15	0.0314	0.0148	0.0308	0.0311
290.15	0.0343	0.0203	0.0324	0.0323
291.15	0.0352	0.0260	0.0340	0.0335
292.15	0.0357	0.0313	0.0358	0.0347
293.15	0.0362	0.0351	0.0377	0.0360
294.15	0.0363	0.0370	0.0397	0.0374
295.15	0.0365	0.0366	0.0418	0.0388
296.15	0.0367	0.0339	0.0441	0.0402
297.15	0.0426	0.0296	0.0466	0.0416
298.15	0.0457	0.0242	0.0492	0.0431

[a] x_1 is the mole fraction solubility of 1,2-Diphenylethane in different solvents; and the standard uncertainty $u(x_1)$=0.005, $u(T)$=0.01K. The experimental pressure is atmospheric pressure.

order is chloroform> dichloromethane>acetone while the mole fraction solubility order is dichloromethane> chloroform> acetone at the temperature from 283.15K to 298.15K. To obtain high output, relatively high solubility is required. Therefore, as solvents, chloroform and dichloromethane are better than acetone and ethanolin solvent crystallization of 1,2-diphenylethane. However, the boiling point of chloroform is higher 21.5 centigrade than that of dichloromethane, and high boiling point can reduce the evaporation loss of solvent during the crystallization process. Since the mole fraction solubility of 1,2-diphenylethane in chloroform are close to that in dichloromethane at the temperature ranging from 278.15K to 298.15K. Combination of the solubility and loss of solvent, chloroform is chosen for the optimal solvent in 1,2-diphenylethane solvent crystallization.

Data correlation

In order to extend the application range of solubility of 1,2-diphenylethane, the experimental solubility data in the several solvents were correlated with the modified Apelblat equation, the semi-empirical Buchowski-Ksiazczak λh equation, and the ideal solution equation.

Modified Apelblat equation

The relationship between 1,2-diphenylethane mole fraction solubility in pure solvent and thermodynamic temperature was described by the modified Apelblat equation[9-12]

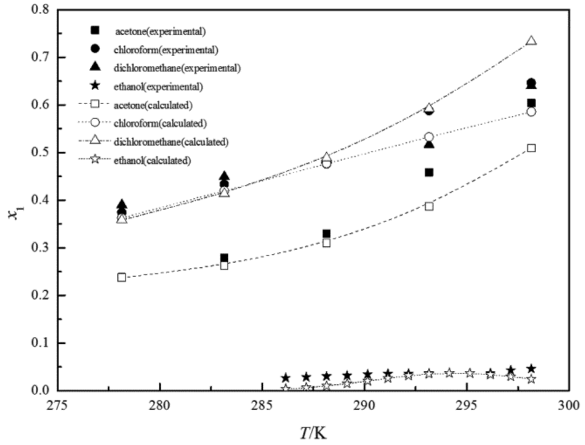

Fig. 2 — Experimental data and calculated Solubilities of 1,2-diphenylethane by modified Apelblat equation

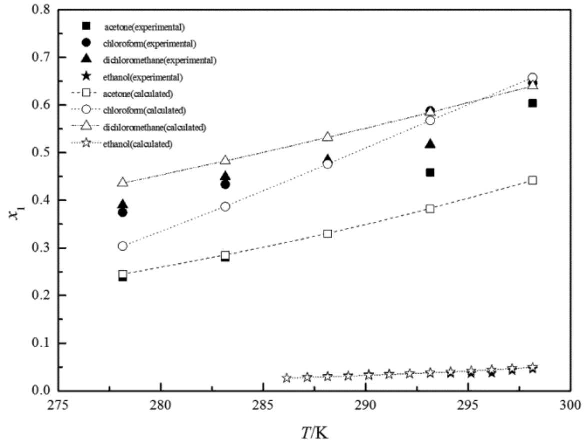

Fig.3 — Experimental data and calculated solubilities of 1,2-diphenylethane by semi-empirical Buchowski-Ksiazczak λh equation

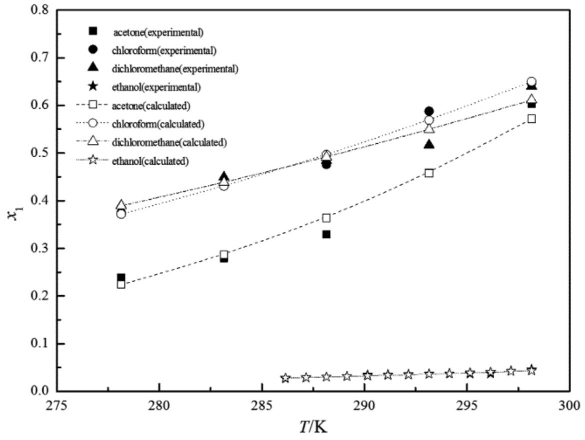

Fig.4 — Experimental data and calculated solubilities of 1,2-diphenylethane by ideal solution equation

Table 3 — Theparameters of modified Apelblat equation for 1,2-diphenylethane in different solvents

Solvent	*a*[a]	*b*	*c*	rmsd
Acetone	-1405.39	57986.79	212.41	0.05427
Chloroform	286.74	-14112.04	-42.113	0.03759
Dichloromethane	-658.23	25894.13	100.23	0.05755
Ethanol	36901.8	-1625563.0	-5520.46	0.01419

[a] *a,b* and *c* are parameters of modified Apelblat equation

$$\ln(x_1) = a + \frac{b}{T/K} + c\ln\left(T/K\right) \qquad \dots(2)$$

Where x_1 is the mole fraction solubility of 1,2-diphenylethane, T is experimental temperature, and a, b, and c are unknown model parameters. The calculating values of mole fraction solubility are also shown in Table 2. The values of a, b, and c with the root-mean-square deviation (rmsd) are listed in Table 3. The rmsd is defined as[13-15]

$$rmsd = \left[\frac{1}{N}\sum_{i=1}^{N}(x_{1,i} - x_{1,i}^{cal})^2\right]^{1/2} \qquad \dots(3)$$

Where N is the number of experimental points, $x_{1,i}$. is the mole fraction solubility of 1,2-diphenylethane of every experimental points, $x_{1,i}^{cal}$ is the calculating value of the mole fraction solubility of every experimental points. The solvents selected in the work, acetone, chloroform, dichloromethane, and ethanol are typical and representative. From Table 3, it can be found that the value of root-mean-square deviationin acetone, chloroform, dichloromethane, and ethanol are less than 0.058. Itis also indicated that the solubilities of 1,2-diphenylethane in the four solvents under the experimental condition can be fitted well with the modified Apelblat equation from Table 3 and Fig.2.

λ*h* equation

The λh equation derived by Buchowski-Ksiazczak can be also employed to describe the solid-liquid equilibrium data[16-17].

$$\ln\left[1 + \frac{\lambda(1-x_1)}{x_1}\right] = \lambda h\left(\frac{1}{T} - \frac{1}{T_m}\right) \qquad \dots(4)$$

where x_1 is the mole fraction solubility of 1,2-diphenylethane, λ and h are the model parameters, T is experimental temperature, T_m is the melting temperature of 1,2-diphenylethane. The Parameters and value of root-mean-square deviation of λ*h* equation for 1,2-diphenylethane in different solvents are listed in Table 4. It can be seen that the value of

Table 4 — Theparameters of λ*h* equation for 1,2-diphenylethane in different solvents

Solvent	λ[a]	*h*	rmsd
Acetone	0.58238	3397.6058	0.08005
Chloroform	6.6119	809.7638	0.03927
Dichloromethane	0.9787	1607.8971	0.04461
Ethanol	0.06157	45706.783	0.00318

[a]*λ* and *h* are parameters of λ*h* equation

Table 5 — Theparameters of ideal solutionequation for 1,2-diphenylethane in different solvents

Solvent	*a*[a]	*b*	rmsd
Acetone	12.485	-3889.2	0.02207
Chloroform	7.3427	-2317.8	0.01260
Dichloromethane	5.7792	-1869.9	0.02027
Ethanol	7.3694	-3134.5	0.00166

[a]*a and b* are parameters of ideal solution equation

rmsd in acetone is more than 0.08 while the values of rmsd in chloroform and dichloromethane are less than 0.045. The value of rmsd in ethanol is less than 0.0032**.** The solubility of 1,2-diphenylethane in chloroform, dichloromethane, and ethanolcan be fitted well with the λh equation under the experimental condition. But the solubility of 1,2-diphenylethanein acetone can not be fitted well with the λh equation under the experimental condition.

Ideal solution equation

The relationship between thermodynamic temperature and mole fraction solubilities of 1,2-diphenylethane is also depicted by the ideal solution equation[18-19].

$$\ln x_1 = a + \frac{b}{T} \qquad \ldots(5)$$

Where x_1 is the mole fraction solubility of 1,2-diphenylethane**,** T is experimental temperature. The Parameters and value of root-mean-square deviationof ideal solution equation for 1,2-diphenylethane in different solvents are listed in Table 5. It is indicated that all the values of root-mean-square deviation are less than 0.023 and the mole fraction solubility of 1,2-diphenylethane can be fitted well with the ideal solutionequationin the four solvents under the experimental condition.

Thermodynamics functions of solution

The apparent molar entropy and enthalpy of solution can be expressed by the Van't Hoff equation[20-22].

$$\ln x_1 = -\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R} \qquad \ldots(6)$$

Table 6 — The enthalpy, entropy and apparent free Gibbs energy of solution in different solvents

Solvent	ΔH_d (kJ·mol^{-1})	ΔS_d (J·mol^{-1}·K^{-1})	ΔG_d (kJ·mol^{-1})
Acetone	32.3348	103.8003	2.4428
Chloroform	19.2792	61.0472	1.6990
Dichloromethane	15.5464	48.0483	1.7096
Ethanol	26.0602	61.269	8.1634

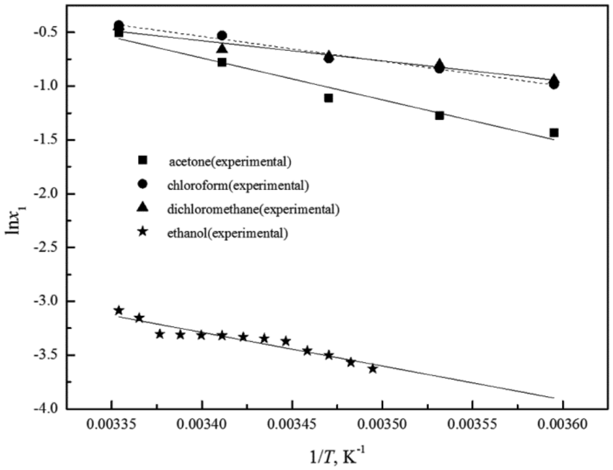

Fig. 5 — Van't Hoff plots of lnx_1 versus $1/T$ in different solvents

where x_1 is the mole fraction solubility of 1,2-diphenylethane, ΔH_d is the solution enthalpy, ΔS_d is the solution entropy, R is the gas constant, R=8.314J·mol^{-1}·K^{-1}, T is experimental temperature. Equation (6) is borrowed to calculated the apparent molar entropy and enthalpy of solution. lnx_1 is taken as ordinate, $1/T$ is taken as horizontal ordinate, and a straight line is realized. ΔH_d is derived from the slope of line and ΔS_d is gotten from the intercept of line. The line were plotted in Fig. 5. The apparent free Gibbs energy of solution ΔG_d can be expressed with the solution enthalpy $\Delta H_d$and solution entropy ΔS_d:

$$\Delta G_d = \Delta H_d - T_{hm} \Delta S_d \qquad \ldots(7)$$

Where T_{hm} is harmonic mean of experimental temperature**,** $T_{hm}=N/\Sigma(1/T_i)$, N is the number of experimental points, T_i is the temperature of every experimental points**.**

The enthalpy, entropy and apparent free Gibbs energy of solution in different solvents are also listed in Table 6. It can be found that ΔH_d of dissolving is positive, which indicated that the dissolving is endothermic. The positive value of ΔS_d is also indicated that the mixing process is also entropy-driving. The values of ΔG_d is positive, which indicated that the dissolving process is not spontaneous.

Conclusion

The mole fraction solubilities of 1,2-diphenylethane in acetone, chloroform, dichloromethane, and ethanol are determined using static equilibrium method from 278.15K to 298.15K (orfrom 286.15K to 298.15K) . For all the solvents selected, the mole fraction solubilities of 1,2-diphenylethane are the function of temperature and increase with temperature. The mole fraction solubility in acetone, chloroform and dichloromethaneare much higher than that in ethanol at the same temperature**.** The solubilities in chloroform and dichloromethane are higher than that in acetone at the temperature ranging from 278.15K to 298.15K. But the boiling point of chloroform is higher 21.5 centigrade than that of dichloromethane, and high boiling point can reduce the loss of solvent. Since the solubilities of 1,2-diphenylethane in chloroform are close to that in dichloromethane at the temperature ranging from 278.15K to 298.15K. Combination of the solubility and loss of solvent, chloroform is chosen for the optimal solvent in 1,2-diphenylethane solvent crystallization. Under the experimental condition, the modified Apelblat,the semi-empirical Buchowski-Ksiazczak λh equation, and the ideal solution equation are well fitted with the experimental data.The enthalpy, entropy and apparent free Gibbs energy of solution in different solvents are calculated. The dissolving process of 1,2-diphenylethane is endothermic, entropy-driving, not spontaneous.

Nomenclature

a,b,c	parameters of model
w_1	the mass fraction of 1,2-diphenylethane in the solution
w_2	the mass fraction of the solvent in the solution
M_1	the molecular weight of 1,2-diphenylethane, $g\cdot mol^{-1}$
M_2	the molecular weight of the solvent, $g\cdot mol^{-1}$
N	the number of experimental points
rmsd	the root-mean-square deviation
R	the gas constant, $8.314 J\cdot mol^{-1}\cdot K^{-1}$
T	the experimental temperature, K
T_i	the temperature of every experimental points, K
T_m	the melting temperature of 1,2-diphenylethane, K
T_{hm}	the harmonic mean of experimental temperature, K
x_1	the mole fraction solubility of 1,2-diphenylethane in different solvents
$x_{1,i}$	the mole fraction solubility of 1,2-diphenylethane of every experimental points
x_1^{cal}	the calculating value of the mole fraction solubilities
$x_{1,i}^{cal}$	the calculating value of the mole fraction solubilitiesof every experimental points
λ, *h*	the model parameters of semi-empirical Buchowski-Ksiazczak λh equation
ΔH_d	the enthalpy of solution, $kJ\cdot mol^{-1}$
ΔS_d	the entropy of solution, $J\cdot mol^{-1}\cdot K^{-1}$
ΔG_d	the apparent free Gibbs energy of solution, $kJ\cdot mol^{-1}$

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