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SHORT ARTICLE

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Measurement and Correlation for the Solubility of Dimethyl 1,4-Cyclohexanedione-2,5-dicarboxylate in Different Solvents at Temperatures from (278.15 to 323.15) K

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ABSTRACT: As an urgent need in the design and upscale of the industrial crystallization process, on the basis of the isothermal saturated method, the solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in *N*,*N*-dimethylformamide, methanol, 1-propanol, acetonitrile, 2-propanol, ethyl acetate, and acetone was measured at atmospheric pressure. The experimental data were well-correlated with the λh model. The calculated solubilities show good agreement with the experimental solubility data. To our knowledge, this is the first time the solubilities of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate are reported.

INTRODUCTION

Dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate(CAS Registry No. 6289-46-9) is a white, almost white, or yellowish white crystalline powder. Its chemical structure is given in Figure 1. Dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate is a multifunctional organic regent, as well as an chemical intermediate with wide use and optimum application prospects in the chemistry industry.[1,2] For example, dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate is a key organic intermediate for pigment quinaridone, which contains high performance pigments of excellent rapidity properties such as lightfastness and heat stability and has been widely used in many areas.[3,4] It also could synthesize some photosensitive materials such as poly[*p*-(2,5-dihydroxy)-phenylenebenzobisoxazole] fiber, polyoxyalkylated colorants, and poly(2,5-bis(*N*-methyl-*N*-hexylamino)phenylene vinylene), which are useful for fluorescent security taggants and light-emitting diodes.[5−7] Furthermore, it could prepare 1,4-cyclohexanedione, which is also an important chemical material as well as an explosive organic regent in the chemistry industry.[8]

The crystallization separation operation is widely used in chemical engineering as a result of low energy consumption and high purity. More particularly, knowledge of an accurate solubility is needed for the design of separation processes such as extractive crystallization[1] or for the safe operation of different processing units such as distillation columns, absorption units, and extraction plants. This data can also supply basic and theoretical data for industrial production.[9−12]

In the purification process of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate, to determine proper solvents and design an optimized production, it is very important to know the solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in different solvents. Unfortunately, no experimental solubility data of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in different solvents are currently available in the literature. In this study, the solubilities of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in *N*,*N*-dimethylformamide, methanol, 1-propanol, acetonitrile, 2-propanol, ethyl acetate, and acetone were measured in the temperature range from (278.15 to 323.15) K so as to provide essential data for the development of crystallization processes. The experimental solubility data were correlated with the λh model.

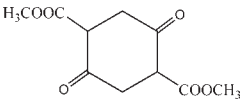

Figure 1. Chemical structure of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate.

EXPERIMENTAL SECTION

Materials. Dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate used during the solubility measurements was purchased from Alfa Aesar. Its purity was greater than 0.9985 in mass fraction, measured by high performance liquid chromatography (HPLC type DIONEX P680, DIONEX Technologies). Its melting point was 327.65 K. The *N*,*N*-dimethylformamide, methanol, 1-propanol, acetonitrile, 2-propanol, ethyl acetate, and acetone for dissolving were of analytical purity grade with a mass fraction purity higher than 0.995 and were supplied by Tianjin Kemel Chemical Reagents Co. All chemicals were used received without further purification.

Apparatus and Procedures. Methods of measuring the solubility of a solid in a solvent can be classified as analytical and synthetic.[13,14] In this work, we adopted the analytical method to determine the solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in the seven solvents with their temperatures ranging from (278.15 to 323.15) K. The advantage of the analytical method is simple and reliable due to the possibility of measuring a large number of samples simultaneously, and its disadvantage is tedious and time-consuming.[15]

The apparatus for solubility measurement was similar to that described in the literature.[16,17] In the experiments, the 10 mL glass test tubes with stoppers were used to prepare saturated solutions(about 8 mL) of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate with excess solid solute in the different solvents. Then the tubes were directly placed in a jacketed vessel

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Table 1. Mole Fraction Solubility of NaCl in Water

	NaCl			
T/K	303.15	313.15	323.15	333.15
x	0.1005	0.1012	0.1023	0.1029
x(lit.)[18]	0.1001	0.1009	0.1019	0.1026
RD	0.0040	0.0030	0.0039	0.0029

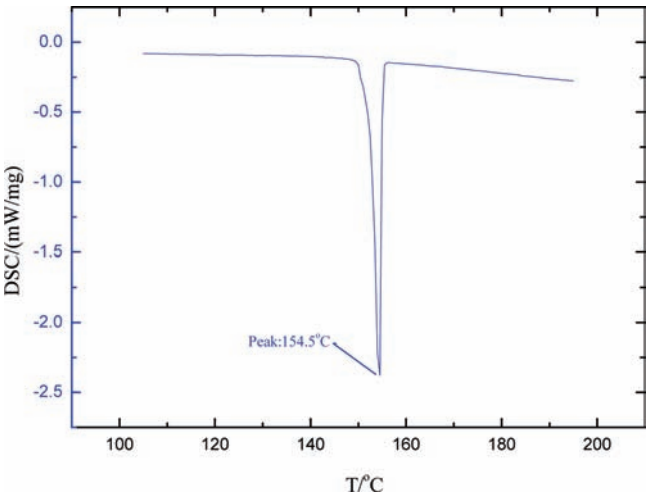

Figure 2. DSC curve of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate.

(1000 mL) with water circulated through the outer jacket from a super thermostatic water-circulator bath (type HWC-52, Shang-Hai Cany Precision Instrument Co., Ltd.) at the required temperature, with a temperature stability of ± 0.05 K and a temperature uncertainty of 0.1 K. A mercury-in-glass thermometer with an uncertainty of ± 0.05 K was inserted into the inner chamber of the vessel to measure the temperature. The contents of the tubes were stirred continuously at certain temperature by a magnetic stirrer. To ensure the solid−liquid equilibrium, the solution was constantly stirred for 12 h at the specified temperature, and then the stirring was stopped to let the solution settle for at least 3 h. A clear liquid (about 1 mL) was put into the sampling vial by a heated pipet. The mass of the sample was determined using an analytical balance with an uncertainty 0.0001 g. Then the clear liquid was quickly filtered though a 0.45 μm membrane. The filtered samples were diluted to an appropriate concentration for HPLC analysis. Triplicate samples were prepared for each data point.

Sample Analysis. The concentration of the dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate was determined using a DIONEX P680 high performance liquid phase chromatograph. The chromatograph column used was Kromasil C18 (250 mm × 4.6 mm, 5 μm), maintained at 303.15 K. A portion of acetonitrile and water in a volume ratio of 80:20 was used as the mobile phase at a flow of 1.00 mL·min^{-1}. The UV wavelength was set at 240 nm, and the injection volume was 20 μL. The calibration curve for estimation of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate was established by using the standard solutions in the appropriate concentration range. The uncertainty of the measurement was less than 0.1 %. Each analysis was repeated three times, and the average value of three measurements was considered the mean value of the analysis. The mean values were

Table 2. Mole Fraction Solubility of Dimethyl 1,4-Cyclohexanedione-2,5-dicarboxylate in Selected Solvents

T/K	10^2 x	10^2 RD	T/K	10^2 x	10^2 RD
		Methanol			
278.15	0.0126	0.99	303.15	0.0535	1.47
283.15	0.0173	1.84	308.15	0.0683	−0.29
288.15	0.0234	2.14	313.15	0.0871	−1.41
293.15	0.0308	0.98	318.15	0.1117	−1.16
298.15	0.0403	0.16	323.15	0.1451	0.94
		Acetonitrile			
278.15	0.0885	0.69	303.15	0.2865	0.08
283.15	0.1154	2.02	308.15	0.3508	−1.22
288.15	0.1464	1.49	313.15	0.4388	0.22
293.15	0.1825	0.02	318.15	0.5314	−1.08
298.15	0.2302	0.36	323.15	0.6608	0.76
		1-Propanol			
278.15	0.0262	1.38	303.15	0.0956	0.87
283.15	0.0343	0.56	308.15	0.1189	−0.92
288.15	0.0444	−0.49	313.15	0.1502	−0.58
293.15	0.0586	1.33	318.15	0.1877	−0.67
298.15	0.0748	0.64	323.15	0.2365	0.61
		Ethyl Acetate			
278.15	0.3035	0.71	303.15	0.9118	0.05
283.15	0.3838	0.59	308.15	1.1049	−0.92
288.15	0.4843	1.05	313.15	1.3559	−0.08
293.15	0.5999	0.36	318.15	1.6256	−1.07
298.15	0.7455	0.69	323.15	1.9961	0.81
		N,*N*-Dimethylformamide			
278.15	0.2482	−0.86	303.15	0.7541	−0.75
283.15	0.3160	−0.35	308.15	0.9345	0.44
288.15	0.3993	0.15	313.15	1.1424	0.80
293.15	0.4924	−1.05	318.15	1.3895	1.17
298.15	0.6131	−0.59	323.15	1.6403	−0.99
		2-Propanol			
278.15	0.1358	−0.85	303.15	0.4857	−1.25
283.15	0.1803	0.18	308.15	0.6242	0.59
288.15	0.2309	−1.43	313.15	0.7869	1.19
293.15	0.3017	−0.22	318.15	0.9759	0.78
298.15	0.3834	−0.97	323.15	1.1894	−0.81
		Acetone			
278.15	0.1896	−0.46	303.15	0.5618	−0.07
283.15	0.2390	−0.33	308.15	0.6883	0.43
288.15	0.2991	−0.22	313.15	0.8336	0.31
293.15	0.3705	−0.39	318.15	1.0068	0.37
298.15	0.4568	−0.40	323.15	1.2008	−0.39

used to calculate the mole fraction solubility x based on

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \quad (1)$$

where m_1 represents the mass of solute and m_2 represents the mass of solvents, respectively. M_1 is the molecular mass of solute; M_2 is the molecular mass of solvents, correspondingly.

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Test of Apparatus. To prove the feasibility and provide the uncertainties of the measurement, the solubilities of NaCl in water were measured and compared with the values reported in the literature.[12,18,19] The experimental measurements agreed with the reported values with a mean relative deviation (RD) of 0.34 %. The measured values are listed in Table 1.

RESULTS AND DISCUSSION

The DSC (differential scanning calorimentry) curve of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate is shown in Figure 2. It can be seen from Figure 2 that melting starts at 426.15 K with a maximum at 427.65 K; only one crystal forms, and there is no other substance in the sample of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate crystalline powder. The melting enthalpy of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate is 116.2 $J \cdot g^{-1}$.

The solubility values of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in methanol, 1-propanol, *N*,*N*-dimethylformamide, acetonitrile, 2-propanol, ethyl acetate, and acetone at different temperatures (T) were measured, and their data are shown in Table 2. The relationship between mole fraction of the solubility and temperature in different pure solvents is described by the λh model, which is a semiempirical equation,[11]

$$\ln\left[1+\frac{\lambda(1-x)}{x}\right] = \lambda h\left[\frac{1}{(T/\mathrm{K})}-\frac{1}{(T_m/\mathrm{K})}\right] \quad (2)$$

where x is the mole fraction of the solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate at the system temperature T, T_m is the normal melting temperature of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate, which can be obtained from the DSC curve of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in Figure 2. λ and h are the model parameters determined by the experimental data in the system together with the root-mean-square deviations (rmsd's) which are listed in Table 3, respectively. The rmsd's are calculated according to:

$$\mathrm{rmsd} = \left[\frac{1}{N}\sum_{i=1}^{N}(x_{ci}-x_i)^2\right]^{1/2} \quad (3)$$

where N is the number of experimental points and x_{ci} and x_i represent the calculated and the experimental solubility values, respectively. The RDs between the calculated and the experimental values are also listed in Table 2. The RDs are calculated according to:

$$\mathrm{RD} = \frac{x-x_c}{x} \quad (4)$$

The relative average deviation (RAD) and the rmsd by eq 2 are also listed in the Table 3. The RAD is defined as follows:

$$\mathrm{RAD} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{x-x_c}{x}\right| \quad (5)$$

The comparison between model predictions according to eq 2 and experimental data is shown in Figure 3. From Table 3 and Figure 3, it can be found that the calculated solubility data show good agreement with the experimental data. Comparing the calculated results of 70 data points according to eq 2 with the experimental ones, the overall rmsd is $0.30 \cdot 10^{-4}$. The RDs by eq 2 among all of these values do not exceed 2.14 %; the RADs are 1.14 %, 0.79 %, 0.80 %, 0.63 %, 0.72 %, 0.85 %, and 0.58 %, respectively, which indicate that the λh model is suitable to correlate the solubility data of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in the selected solvents.

Table 3. Parameters of eq 2 for Dimethyl 1,4-Cyclohexanedione-2,5-dicarboxylate in Pure Solvents

solvent	λ	h	10^4 rmsd	10^2 RAD
methanol	0.0543	89019.8981	0.07	1.14
acetonitrile	0.1228	32039.8864	0.03	0.79
1-propanol	0.0605	71753.1195	0.01	0.80
ethyl acetate	0.3081	11968.8549	0.09	0.63
N,*N*-dimethylformamide	0.2588	14284.1415	0.08	0.72
2-propanol	0.3227	13549.3666	0.01	0.85
acetone	0.1687	21165.9416	0.01	0.58

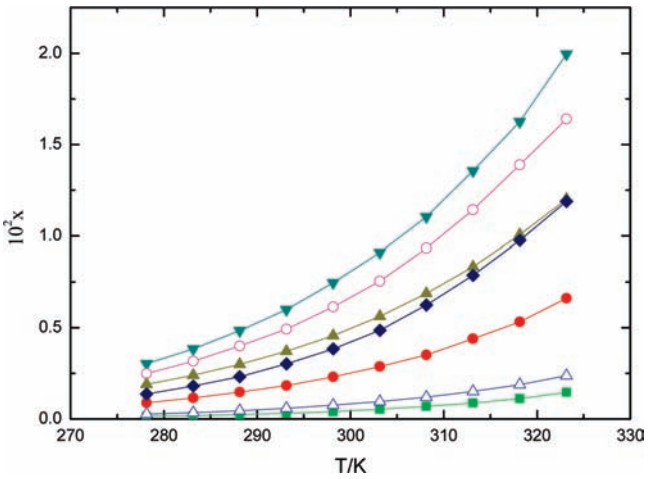

Figure 3. Mole fraction solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in different solvents between (278.15 to 323.15) K: ▼, ethyl acetate; ◆, *N*,*N*-dimethylformamide; ▲, acetone; ○, 2-propanol; ●, acetonitrile; △, 1-propanol; ■, methanol. Solid line, calculated from eq 2.

From the results shown in Table 2 and Figure 3, it can be seen that the solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate increases with the increase in the temperature from (278.15 to 323.15) K. The solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in these solvents decreased in the sequence ethyl acetate, *N*,*N*-dimethylformamide, acetone, 2-propanol, acetonitrile, 1-propanol, and methanol. Among these solvents, the solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate is the highest in ethyl acetate and the lowest in ethyl methanol; the solubility in ethyl acetate increased most significantly with the increasing temperature. The result showed that the polarity of the solvent is not the only factor to determine the solubility, as the solvents' polarity is in the following order: acetonitrile > *N*,*N*-dimethylformamide > methanol acetone > 1-propanol > 2-propanol > ethyl acetate.[20] We can see from Figure 1 that there is a ring structure, which has two ester groups and two acylradicals in the dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate molecule, and ethyl acetate has a ester group, so the structure similarity between the solvent and the solute due to the ester group enhanced the solubility significantly, corresponding to the empirical rule "like dissolves like" to ethyl acetate. In

addition, based on the Lewis theory, *N*,*N*-dimethylformamide is an alkaline aprotic solvent, which enhances the solvent effect between dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate and *N*,*N*-dimethylformamide molecules and promotes the solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in *N*,*N*-dimethylformamide. The solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate is lowest in the two primary alcohols, methanol and 1-propanol; this may be caused by the formation of cavities. To solubilize a molecule, one must create a cavity in the solvent wherein the solute will reside. In the case of methanol (and other self-associated solvent molecules), one must break solvent−solvent hydrogen bonds, which are endothermic. One does regain part of the enthalpy if the solute were to form hydrogen bonds with surrounding solvent molecules.

CONCLUSIONS

The solubility of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate in *N*,*N*-dimethylformamide, methanol, 1-propanol, acetonitrile, 2-propanol, ethyl acetate, and acetone was measured at atmospheric pressure in the temperature range from (278.15 to 323.15) K by an analysis method. The λh model was used to fit the experimental data. The overall rmsd is $0.30 \cdot 10^{-4}$, and it can be seen that the solubility calculated by the λh model shows good agreement with experimental values. The experimental solubility and correlation in this work can be used as essential data and models in the purification process of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate.

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