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Solubility of Glutaric Acid in Cyclohexanone, Cyclohexanol, Their Five Mixtures and Acetic Acid

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Abstract By using the laser-monitoring technique, solid-liquid equilibrium data of glutaric acid in cyclohexanol, cyclohexanone, their five mixed solvents and acetic acid were measured within the temperature range from 292.15K to 354.60K by dynamic method**.** Empirical formula and λh equation were used to correlate the solubilities of glutaric acid in eight solvents. The maximal average relative deviations were 1.15% and 2.20% by using the empirical formula and λh equation to correlate the solubility data. The results showed that the empirical formula and λh model could correlate the solubility data of glutaric acid in eight solvents. In addition, the solubility data of glutaric acid in five mixtures (cyclohexanone+cyclohexanol) could be predicted with the NRTL equation utilizing the parameters of the binary systems. The total average relative deviation was 3.60%. The results indicate that the NRTL equation could well predict the solubilities of glutaric acid in the mixed solvents of cyclohexanone and cyclohexanol.
Keywords glutaric acid, solid-liquid equilibrium, solubility, λh equation, NRTL equation

1 INTRODUCTION

Adipic acid is an important chemical, whose production is necessary for the manufacture of nylon-66[1—3]. Adipic acid can be synthesized with cyclohexane as raw material. Glutaric acid is an important chemical industry material for producing a wide range of industrial chemicals. Therefore, the recovery of glutaric acid from dicarboxylic acid mixture , which consists of glutaric acid, adipic acid, and succinic acid, from waste alkali liquid in cyclohexane oxidation is essential not only because of the considerable economic efficiency，but also the positive contributions to the environment.

Solubility is an important basic property of solid–liquid equilibrium (SLE) in the chemical industry. Such data are required for the proper design and optimization of various chemical processes[4]. However, the solubilities of glutaric acid are nearly unavailable, except in water and benzene. The industrial production of adipic acid uses nitric acid oxidation of cyclohexanol or a cyclohexanol/cyclohexanone mixture[5]. In addition, acetic acid is an organic solution that is used extensively. Therefore, the solubilities of glutaric acid in cyclohexanone, cyclohexanol, their mixtures, and acetic acid were determined and correlated in this study. The results showed that the empirical formula, λh equation, and NRTL equation could correlate the solubility data of glutaric acid well. In addition, the solubility data of glutaric acid in five mixtures (cyclohexanone+cyclohexanol) could be predicted with the NRTL equation utilizing the parameters of the binary systems. At the higher temperature, the predicted solubiliy data of glutaric acid in five mixtures was consistent with the experimental solubilities. However, at the lower temperature, the experimental data are larger than the predicted data because of the interaction between molecules in the mixtures.

2 EXPERIMENTAL

2.1 Materials

All materials used in the experiments are of analytical grade purity and the information on glutaric acid, adipic acid, cyclohexanone, cyclohexanol and acetic acid is shown in Table 1.

2.2 Apparatus and procedure

By using laser monitoring technique, the solubility was determined by the dynamic method[6]. Compared with the conventional synthetic methods[7,8], the dissolving process was observed visually. The characteristic of this method is that optics and chemis-

Table 1 Information of the applied materials

Material	Purity (mass fraction), %	Manufacturing plant	Material	Purity (mass fraction), %	Manufacturing plant
adipic acid	99.8	Tianjin Guangfu Fine Chemical Research Institute	cyclohexanol	99.0	Tianjin Bodi Chemicals Company
glutaric acid	99.0	Tianjin Guangfu Fine Chemical Research Institute	acetic acid	99.5	Kewei Company of Tianjin University
cyclohexanone	99.5	Damao Chemical Reagent Factory			

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try principles are combined, so that it is more helpful in getting SLE data, especially for low solubilities. During the experiments, the dissolving processes were indirectly observed by a laser[9]. The experimental apparatus included a SLE cell of 100cm^3 volume, temperature controlling and measurement with a precision of $\pm$0.01K, a laser detecting system consisting of laser emitter, photoelectric transformer and galvanometer, and a magnetic stirring system, as shown in Fig.1.

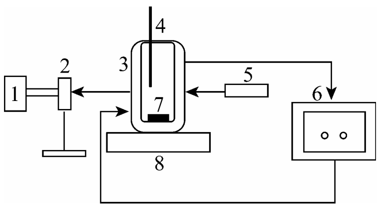

Figure 1 The experimental apparatus for determining solubility
1—galvanometer; 2—photoelectric transformer; 3—solubility cell; 4—thermometer; 5—laser emitter; 6—temperature control device; 7—stirring magnetic iron; 8—magnetic stirring system

Every sample, such as glutaric acid and all solvents, was weighed respectively by electrical balance with precision of $\pm$0.0001g. A predetermined sample was put into the solubility cell and heated very slowly. The rate of increasing temperature was controlled, especially near the SLE temperature, in less than 0.2K·h^{-1}. The power of the laser that went through the sample increased as the solid decreased. When the last piece of solid disappeared, the laser power reached the largest value. The power of laser was converted into electrical signal and detected by the galvanometer. The temperature corresponding to the largest value of the galvanometer was the SLE temperature of the sample[6].

To verify the reliability of the experimental apparatus, solubility of adipic acid in water was measured and compared with the literature[10]. The result agreed well with the solubility data in the literature, as shown in Fig.2.

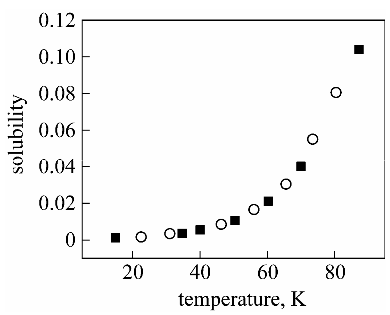

Figure 2 Solubility of adipic acid in water
○ experimental solubility values;
■ solubility values in literature

3 RESULTS AND DISCUSSION

3.1 Experimental results

The solubilities of glutaric acid in cyclohexanone, cyclohexanol, the five mixtures (cyclohexanone+cyclihexanol), and acetic acid were determined in this article and listed in Table 2 and Table 3. The temperature range was from 292.15K to 354.60K. The mole fraction of glutaric acid is x.

Table 2 Experimental solubility data of glutaric acid in cyclohexanone, cyclohexanol, and acetic acid

Cyclohexanone		Cyclohexanol		Acetic acid	
T, K	x	T, K	x	T, K	x
294.00	0.1612	299.75	0.2053	292.75	0.1624
299.70	0.1891	302.70	0.2190	297.84	0.1828
304.50	0.2129	305.85	0.2338	301.30	0.2034
308.05	0.2411	308.60	0.2497	304.47	0.2210
311.94	0.2642	313.19	0.2713	307.28	0.2410
314.15	0.2835	316.00	0.2883	310.19	0.2573
317.54	0.3070	318.55	0.3121	313.64	0.2800
320.30	0.3336	320.55	0.3302	316.50	0.3017
325.05	0.3660	325.15	0.3659	319.05	0.3225
326.95	0.3921	326.50	0.3714	321.38	0.3448
330.50	0.4276	332.55	0.4277	325.45	0.3735
333.81	0.4578	334.90	0.4552	327.38	0.3994
335.23	0.4776	336.30	0.4769	332.97	0.4363
338.35	0.5126	339.75	0.5114	335.25	0.4785
342.65	0.5573	342.15	0.5452	338.05	0.5136
346.80	0.5983	344.80	0.5712	341.94	0.5526
347.65	0.6273	347.19	0.6223	344.21	0.5847
349.70	0.6552	350.05	0.6603	347.24	0.6214
351.50	0.6795	351.93	0.6926	349.88	0.6515
353.65	0.7053	352.48	0.7187	353.36	0.7120
		352.95	0.7476		

3.2 Correlation with empirical formula, λh equation, and NRTL equation

3.2.1 *Empirical formula*

For a determined system, temperature is one of the most important factors to influence the solubility. Empirical formula used in this work can be written as

$$x = AT^3 + BT^2 + CT + D \quad (1)$$

The parameters (A, B, C, D) of empirical formula were correlated with experimental data. Relativity coefficient (R^2) exceeded 0.998. The average relative deviation (ARD) between the experimental and calculated mole fraction of glutaric acid was defined as

$$\text{ARD} = \frac{1}{n} \times \sum \left| \frac{x_{\text{exp}} - x_{\text{cal}}}{x_{\text{exp}}} \right| \times 100\% \quad (2)$$

The correlation parameters of the empirical formula are shown in Table 4.

The results showed that empirical formula could correlate the solubility data of glutaric acid in eight solvents.

3.2.2 *λh equation*

λh equation is an equation which was first put

Table 3 Experimental solubility data of glutaric acid in cyclohexanol + cyclohexanone mixtures

1∶9[①]		3∶7[①]		5∶5[①]		7∶3[①]		9∶1[①]	
T, K	x	T, K	x	T, K	x	T, K	x	T,K	x
295.05	0.1831	292.45	0.1872	292.88	0.1884	294.15	0.1896	292.15	0.1693
300.85	0.2081	298.40	0.2082	297.45	0.2131	298.94	0.2144	295.24	0.1855
304.55	0.2308	302.58	0.2326	300.05	0.2256	304.50	0.2351	300.65	0.2063
308.61	0.2532	308.02	0.2546	304.05	0.2430	307.37	0.2536	305.45	0.2241
314.55	0.2970	314.65	0.2933	308.30	0.2620	311.65	0.2744	308.20	0.2418
318.25	0.3208	318.35	0.3268	311.80	0.2850	316.50	0.3036	312.24	0.2642
321.34	0.3454	323.24	0.3598	317.90	0.3175	319.15	0.3260	315.75	0.2873
325.35	0.3768	327.95	0.4008	322.82	0.3518	323.25	0.3585	319.20	0.3134
328.30	0.4043	332.00	0.4358	327.25	0.3922	327.15	0.3937	322.65	0.3467
331.50	0.4376	334.35	0.4683	330.77	0.4293	330.91	0.4292	326.65	0.3767
334.47	0.4688	339.00	0.5143	334.95	0.4738	334.55	0.4678	331.65	0.4306
338.04	0.5066	342.50	0.5598	338.45	0.5133	338.03	0.5133	335.75	0.4760
342.00	0.5486	345.45	0.5999	342.00	0.5564	343.35	0.5756	339.15	0.5152
345.59	0.5992	348.94	0.6432	345.55	0.6002	347.28	0.6243	343.65	0.5733
348.90	0.6418	352.35	0.6911	349.65	0.6532	351.95	0.6862	347.65	0.6249
352.52	0.6919			351.66	0.6884	354.30	0.7253	350.54	0.6563
354.60	0.7224			354.15	0.7166			352.50	0.7079

① The mass ratio is cyclohexanol to cyclohexanone, the same as in Table 4 and Table 5.

Table 4 Correlation parameters of empirical formula and average relative deviations

Solvent	$A\times10^7$	$B\times10^5$	$C\times10^4$	$D\times10^3$	R^2	ARD, %
cyclohexanone	2.0511	4.9665	23.600	87.630	0.9994	0.74
cyclohexanol	19.863	18.453	112.10	3.1300	0.9982	1.07
acetic acid	2.7176	5.0114	16.300	115.20	0.9988	1.15
1:9	3.9790	2.6321	28.200	103.54	0.9999	0.43
3:7	3.7911	4.0600	13.400	144.04	0.9997	0.66
5:5	4.7041	2.8860	16.900	145.99	0.9995	0.98
7:3	1.3334	7.9833	4.9227	167.55	0.9997	0.68
9:1	2.5652	6.6152	1.1159	144.76	0.9994	0.86

forward for SLE by Buchowski[11] in 1980. λh equation are able to deal with strong polarity systems. There are two parameters (λ and h) in this equation.

The λh equation could be extended to correlate the solubilities of solids in mixed solvents[12]. Every mixture (cyclohexanol+cyclohexanone) was considered as a new solvent when the solubility data of glutaric acid in five mixed solvents were correlated. The correlated results showed that calculated data was consistent with experimental data on the whole. λh equation can be expressed as

$$\ln\left[1+\frac{\lambda(1-x)}{x}\right]=\lambda h\left(\frac{1}{T}-\frac{1}{T_{\mathrm{m}}}\right) \tag{3}$$

The experimental data and correlated data with λh are shown in Fig.3.The correlation parameters of λh equation are shown in Table 5.

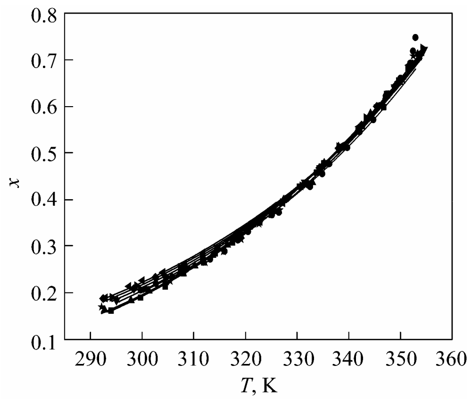

Figure 3 The comparison of experimental data with calculated data with λh model
■ cyclohexanone; ● cyclohexanol; ▲ acetic acid; ▼ 1∶9; ◆ 3∶7; ◀ 5∶5; ▶ 7∶3; ★ 9∶1; — calculated data

Table 5 Correlation parameters of λh equation and average relative deviations

Solvent	λ	h	ARD, %
cyclohexanone	1.03136	2544.407	0.73
cyclohexanol	0.73166	2909.375	2.20
acetic acid	0.99140	2569.180	0.84
1:9	0.86080	2680.764	0.60
3:7	0.68478	2850.506	1.60
5:5	0.64064	2880.268	1.77
7:3	0.75309	2788.188	1.79
9:1	0.88313	2730.143	2.18

3.2.3 *NRTL equation*

NRTL equation[13] can be applied to predict the characters of ternary and multicomponent systems utilizing the parameters of the binary systems. In solid-liquid coexisting phases, fugacities of i in solid is equal to that in liquid at SLE. The following well-known simplified equation can be obtained through thermodynamics cycle and rational hypothesis.

$$\ln \gamma_i x_i = -\frac{\Delta_m H_i}{R}\left(\frac{1}{T} - \frac{1}{T_{mi}}\right) \tag{4}$$

Normal melting temperature T_{mi} and fusion enthalpy $\Delta_m H_i$ can be obtained in literature[14]. $\Delta_m H_i$=20900J·mol^{-1}, T_{mi}=371.15K.

NRTL equation can be expressed as follows:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_j G_{ji} x_j} + \sum_j \frac{G_{xj} x_j}{\sum_k G_{kj} x_k}\left(\tau_{ij} - \frac{\sum_k \tau_{kj} G_{kj} x_k}{\sum_k G_{kj} x_k}\right) \tag{5}$$

$$\tau_{ji} = \left(g_{ji} - g_{ii}\right)/RT \tag{6}$$

$$G_{ji} = \exp\left(-\alpha_{ji}\tau_{ji}\right) \tag{7}$$

$$\alpha_{ji} = \alpha_{ij} \tag{8}$$

For ternary system, the parameters include $g_{21}-g_{11}$, $g_{31}-g_{11}$, $g_{12}-g_{22}$, $g_{32}-g_{22}$, $g_{13}-g_{33}$, $g_{23}-g_{33}$, α_{12}, α_{13} and α_{23} (1-glutaric acid,2-cyclohexanone,3-cyclohexanol). $g_{23}-g_{33}$, $g_{32}-g_{22}$ and α_{23} can be obtained in literature[15]. $g_{12}-g_{22}$, $g_{21}-g_{11}$, α_{12}, $g_{13}-g_{33}$, $g_{31}-g_{11}$ and α_{13} can be correlated by using the experimental solubility data of glutaric acid in cyclohexanone and cyclohexanol respectively. The parameters of NRTL equation are shown in Table 6.

The experimental data and calculated data of eight solvents with NRTL are shown in Fig.4.

The average relative deviations (ARD) between the experimental and calculated mole fraction of glutaric acid in three pure solvents are shown in Table 7. The average relative deviations of ternary system (glutaric acid + cyclohexanone + cyclohexanol) predicted with NRTL equation are showed in Table 8.

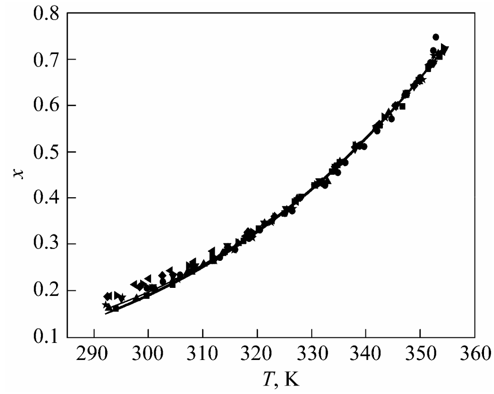

Figure 4 The comparison of experimental data with calculated data with NRTL model
■ cyclohexanone; ● cyclohexanol; ▲ acetic acid; ▼ 1∶9; ◆ 3∶7; ◄ 5∶5; ► 7∶3; ★ 9∶1; — calculated data

Table 7 Average relative deviations with NRTL equation in pure solvents

Solvent	ARD, %
cyclohexanone	0.72
cyclohexanol	2.67
acetic acid	0.67

Table 8 The predicted results in five mixed solvents with NRTL equation

Solvent	ARD, %
1∶9	2.21
3∶7	4.08
5∶5	5.16
7∶3	4.02
9∶1	2.52

The results showed that NRTL equation could well predict the solubilities of glutaric acid in the mixed solvent of cyclohexanone and cyclohexanol.

4 CONCLUSIONS

(1) An apparatus for determining solubilities of glutaric acid in cyclohexanone, cyclohexanol, their five mixtures, and acetic acid by dynamic method has been designed and established with a laser detection system.

(2) The solubilities were determined at the temperature range from 292.15K to 354.60K. The solubilities of glutaric acid in eight solvents increased with the increasing of temperature according to the experimental data. The dissolving capacity of glutaric

Table 6 Parameters of NRTL equation in binary system

Solute	$g_{21}-g_{11}$	$g_{31}-g_{11}$	$g_{12}-g_{22}$	$g_{32}-g_{22}$	$g_{13}-g_{33}$	$g_{23}-g_{33}$	α_{12}	α_{13}	α_{23}
glutaric acid	92.19	118.6	88.81	128.8	132.1	−130.3	0.2266	0.0211	0.3028

acid in eight different solvents is similar.

(3) The results showed that empirical formula and λh equation could correlate the solubility data of glutaric acid in eight solvents well, and NRTL equation could predict the solubilities of glutaric acid in the mixed solvents of cyclohexanone and cyclohexanol well.

NOMENCLATURE

A, B, C, D	parameters in empirical formula
ARD	average relative deviation, %
$g_{ji}-g_{ii}$	parameters in NRTL equation
$\Delta_m H_i$	fusion enthalpy, $J\cdot mol^{-1}$
h	parameter in λh equation, K
h_i	parameter of pure solvent i in λh equation , K
n	number of experimental solubility data
R	universal gas constant, $J\cdot mol^{-1}\cdot K^{-1}$
R^2	relativity coefficient of empirical formula
T	experimental temperature, K
T_m	melting temperature of solute, K
T_{mi}	normal melting temperature, K
x	mole fraction of succinic acid
α	nonrandom parameter in NRTL equation
γ	activity coefficient of succinic acid
λ	parameter in λh equation
λ_i	parameter of pure solvent i in λh equation

Subscripts

cal	calculated result
exp	experimental result
i, j, k	component
1	glutaric acid
2	cyclohexanone
3	cyclohexanol

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