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Solubility of 4-(3,4-dichlorophenyl)-1-tetralone in ethanol and acetone mixtures with the temperature range from 283.15 to 323.15 K

Shui Wang†, Qun-Sheng Li and Zhao Li

College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China
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Abstract−The solubility of 4-(3,4-dichlorophenyl)-1-tetralone in the mixture of ethanol and acetone was measured by using a laser technique in the temperature range from 283.15 to 323.15 K. The results were correlated with a semi-empirical equation. The experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of 4-(3,4-dichlorophenyl)-1-tetralone.

Key words: 4-(3,4-Dichlorophenyl)-1-Tetralone, Laser Technique, Solubility

INTRODUCTION

4-(3,4-Dichlorophenyl)-1-tetralone (molecular formula $C_{16}H_{12}Cl_2O$, CAS Registry No. 79560-19-3, molecular weight 291.17) is a kind of white or almost white crystalline powder. The molecular structure of 4-(3,4-dichlorophenyl)-1-tetralone see Fig. 1. As an intermediate, 4-(3,4-dichlorophenyl)-1-tetralone has been widely used in synthesis of sertraline hydrochloride which is a very effective antidepressant. While 4-(3,4-dichlorophenyl)-1-tetralone is undissolved in water, some organic solvents such as ethanol, acetone, toluene, THF and so on are employed in the production of sertraline hydrochloride. To determine proper solvents and design an optimized production process, it is necessary to measure the solubility of 4-(3,4-dichlorophenyl)-1-tetralone in different solvents. However, it was found that no experimental solubility data were available from the literature. In this paper, the solubility of 4-(3,4-dichlorophenyl)-1-tetralone in the mixture of ethanol+acetone was experimentally determined at the temperature range from 283.15 to 323.15 K. The experimental method employed in this work was classed as a synthetic method, which was much faster and more readily than the analytical method.

EXPERIMENTAL SECTIONS

1. Materials

An almost white crystalline powder of 4-(3,4-dichlorophenyl)-1-tetralone was purchased from Jiangsu Chemstar Industries Ltd. The mass fraction purity determined by HPLC was higher than 99.2%. Ethanol and acetone were analytical research grade reagent from Beijing Chemical Reagent Co.

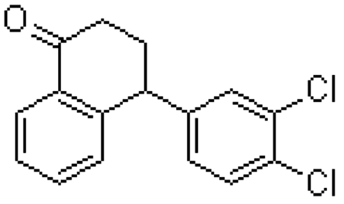

Fig. 1. The molecular structure of 4-(3,4-dichlorophenyl)-1-tetralone.

2. Apparatus and Procedures

The solubility of 4-(3,4-dichlorophenyl)-1-tetralone was measured by using an apparatus similar to that described as literature. A 100 and 250 mL jacketed vessel was used to determine the solubility. The temperature was controlled to be constant (fluctuates with 0.05 K) through a thermostat water bath. The dissolution of the solute was examined by a laser beam penetrating the vessel. To prevent the evaporation of the solvent, a condenser vessel was introduced. The masses of the samples and solvents were weighted with an analytical balance (Sartorius CP124S, Germany) with an uncertainty of ±0.0001 g.

The solubility of 4-(3,4-dichlorophenyl)-1-tetralone was determined by using a laser technique. During experiments the fluid in the glass vessel was monitored by a laser beam. Predetermined excess amounts of solvent and 4-(3,4-dichlorophenyl)-1-tetralone of known mass were placed in the inner chamber of the vessel. The contents of the vessel were stirred continuously at a given temperature. In the early stage of the experiment, the laser beam was blocked by the undissolved particles of 4-(3,4-dichlorophenyl)-1-tetralone in the solution, so the intensity of the laser beam penetrating the vessel was lower. Along with the dissolution of the particles of the solute, the intensity of the laser beam increased gradually. When the solute dissolved completely, the solution was clear and transparent, and thus the laser intensity reached maximum. Then additional solute of known mass (about 1-5 mg) was added into the vessel. This procedure was repeated until the penetrated laser intensity could not return maximum. This indicates that the last addition of solute could not dissolve completely. The interval of addition was 30 min. The total amount of the solute consumed was recorded. The same solubility experiment was conducted three times, and the mean values were used to calculate the mole fraction solubility (x_1) based on Eq. (1). The composition of solvent mixture (x_2') was defined as Eq. (2):

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \tag{1}$$

†To whom correspondence should be addressed.
E-mail: lantianxia2005@sohu.com

$$x_2' = \frac{m_2/M_2}{m_2/M_2 + m_3/M_3} \tag{2}$$

where m_1, m_2, and m_3 represent the mass of the solute, acetone and ethanol, respectively, and M_1, M_2, and M_3 are the molecular weight of the solute, acetone and ethanol, respectively.

RESULTS AND DISCUSSION

The solubilities of 4-(3,4-dichlorophenyl)-1-tetralone in the mixture of ethanol and acetone at different temperatures are shown in Table 1.

The solubility of a solid in a liquid may be expressed in a general manner as

$$\ln x_1 = \frac{\Delta H_{f,1}}{RT_{f,1}}\left(\frac{T_{f,1}}{T}-1\right) - \frac{\Delta C_{pf,1}}{R}\left(\frac{T_{f,1}}{T}-1\right) + \frac{\Delta C_{pf,1}}{R}\ln\frac{T_{f,1}}{T} - \ln\gamma_1 \tag{3}$$

Where x_1, γ_1, $\Delta H_{f,1}$, $\Delta C_{pf,1}$, $T_{f,1}$, R, and T stand for the mole fraction of the solute, activity coefficient, enthalpy of fusion, difference in the solute heat capacity between the solid and liquid at the melting temperature, melting temperature of the solute, gas constant, and equilibrium temperature in the saturated solution, respectively. For regular solutions, the activity coefficient is given by

$$\ln\gamma_1 = A + \frac{B}{T} \tag{4}$$

where A and B stand for empirical constants. Incorporating γ_1 from Eq. (4) into Eq. (3) and subsequent rearrangements results in Eq. (5):

Table 1. Solubility (x_1) of 4-(3,4-Dichlorophenyl)-1-Tetralone in the ethanol (2)+acetone (3) mixture at the temperature range from 283.15 K to 323.15 K

T/K	$10^3\ x_1$	$10^3\ x_1^{calc}$	$10^3\ (x_1-x_1^{calc})$	T/K	$10^3\ x_1$	$10^3\ x_1^{calc}$	$10^3\ (x_1-x_1^{calc})$
			$x_2'=0.0000$				
282.13	16.1621	16.6763	−0.5142	307.94	49.7982	50.6495	−0.8513
288.02	21.6826	20.8902	0.7924	313.74	67.2653	67.5738	−0.3085
292.83	26.0577	25.4477	0..6100	318.56	87.1339	86.6318	0.5021
298.28	32.1230	32.2516	−0.1286	323.57	114.0034	113.0425	0.9609
303.23	39.7378	40.4518	−0.7140				
			$x_2'=0.1229$				
283.27	14.6533	15.1448	−0.4915	308.18	44.7973	46.2466	−1.4493
288.21	19.0974	18.5493	0.5481	313.26	59.5010	59.5465	−0.0455
293.17	23.5855	22.9668	0.6187	318.19	77.1735	76.6110	0.5625
298.26	29.4526	28.8724	0.5802	323.21	100.6426	99.6381	1.0045
303.17	35.4017	36.3115	−0.9098				
			$x_2'=0.2396$				
283.17	12.8595	13.1742	−0.3147	308.16	39.3460	40.5016	−1.1556
288.16	16.4792	16.2253	0.2539	313.21	51.6014	51.9029	−0.3015
293.18	20.4521	20.1831	0.2690	318.16	66.9740	66.5598	0.4142
298.19	26.5517	25.2968	1.2549	323.17	87.0835	86.0579	1.0256
303.26	30.9173	32.0304	−1.1131				
			$x_2'=0.3508$				
283.25	11.0313	11.214	−0.1827	308.16	33.8022	34.4475	−0.6453
288.29	13.9728	13.8612	0.1116	313.27	43.8810	44.2478	−0.3668
293.17	17.3774	17.1541	0.2233	318.20	56.9662	56.6357	0.3305
298.26	22.3540	21.5892	0.7648	323.22	73.8522	73.1755	0.6767
303.18	26.4731	27.1476	−0.6745				
			$x_2'=0.4567$				
283.17	9.2222	9.3330	−0.1108	308.19	28.3155	28.6019	−0.2864
288.19	11.6071	11.4936	0.1135	313.17	36.4804	36.5153	−0.0349
293.29	14.4209	14.3321	0.0888	318.28	47.3442	47.1990	0.1452
298.28	18.3001	17.9338	0.3663	323.26	61.1935	60.9378	0.2557
303.26	22.1550	22.5981	−0.4431				
			$x_2'=0.5577$				
283.18	7.4856	7.5646	−0.0790	308.22	23.0353	23.1586	−0.1233
288.21	9.4112	9.3065	0.1047	313.27	29.5400	29.6987	−0.1587
293.26	11.6417	11.5694	0.0723	318.18	38.3017	38.0547	0.2470
298.2	14.5035	14.4376	0.0659	323.19	49.3524	49.2875	0.0649
303.19	18.0492	18.2008	−0.1516				

Table 1. Continued

T/K	10^3 x_1	10^3 x_1^{calc}	10^3 $(x_1-x_1^{calc})$	T/K	10^3 x_1	10^3 x_1^{calc}	10^3 $(x_1-x_1^{calc})$
			$x_2'=0.6541$				
283.17	5.8750	5.9271	−0.0521	308.19	18.1110	18.0793	0.0317
288.34	7.4138	7.3226	0.0912	313.16	23.2005	23.1145	0.0860
293.16	9.0991	9.0045	0.0946	318.3	30.0329	30.0081	0.0248
298.18	11.0780	11.2706	−0.1926	323.16	38.5737	38.6365	−0.0628
303.29	14.2415	14.2894	−0.0479				
			$x_2'=0.7463$				
283.17	4.4437	4.4916	−0.0479	308.17	13.692	13.5986	0.0934
288.18	5.6439	5.4925	0.1514	313.16	17.6023	17.4327	0.1696
293.31	6.8525	6.8281	0.0244	318.21	22.7316	22.5858	0.1458
298.19	8.1372	8.4843	−0.3471	323.22	29.1022	29.4067	−0.3045
303.26	10.8180	10.7347	0.0833				
			$x_2'=0.8345$				
283.29	3.2452	3.2903	−0.0451	308.18	9.9278	9.8532	0.0746
288.17	4.1304	3.9871	0.1433	313.19	12.8858	12.6732	0.2126
293.2	4.9611	4.9220	0.0391	318.22	16.5918	16.458	0.1338
298.22	5.7945	6.1457	−0.3512	323.20	21.1829	21.4862	−0.3033
303.27	7.8647	7.7689	0.0958				
			$x_2'=0.9190$				
283.17	2.2787	2.2137	0. 0650	308.18	6.8858	6.7386	0. 1472
288.40	2.6573	2.7076	−0.0503	313.23	9.0070	8.7872	0.2198
293.28	3.2245	3.3204	−0.0959	318.17	11.6218	11.5187	0.1031
298.16	4.0614	4.1309	−0.0695	323.16	14.8704	15.2968	−0.4264
303.26	5.2910	5.2648	0.0262				
			$x_2'=1.0000$				
283.12	1.7150	1.7309	−0.0159	308.32	0.004.9024	0.004.9122	−0.0098
288.27	2.0993	2.0659	0.0334	314.17	0.006.6686	0.006.6192	0.0494
293.38	2.5236	2.5116	0.0120	318.74	0.008.5181	0.008.4591	0.0059
298.04	3.0282	3.0495	−0.0213	323.26	0.010.8252	0.010.8881	−0.0629
302.93	3.7593	3.7954	−0.0361				

$$\ln x_1=\left[\frac{\Delta H_{f,1}}{RT_{f,1}}+\frac{\Delta C_{pf,1}}{R}(1+\ln T_{f,1})-A\right]-\left[B+\left(\frac{\Delta H_{f,1}}{RT_{f,1}}+\frac{\Delta C_{pf,1}}{R}\right)T_{f,1}\right]\frac{1}{T}-\frac{\Delta C_{pf,1}}{R}\ln T \quad (5)$$

Eq. (5) can be rewritten as

$$\ln x_1=a+\frac{b}{T}+c\ln T \quad (6)$$

where T is the absolute temperature, and a, b, and c are empirical constants.

The solubility data are correlated with Eq. (6). The deviation between experimental and correlated results is presented in Table 1. The values of the three parameters a, b, and c together with the root-mean-square deviations (RMSD) are listed in Table 2 where the RMSD is defined by

$$RMSD=\left[\frac{\sum_{j=1}^{N}(x_{1,j}-x_{1,j}^{calc})^2}{N-1}\right]^{1/2} \quad (7)$$

Table 2. Parameters of Eq. (6) for 4-(3,4-Dichlorophenyl)-1-Tetralone in the mixture of ethanol and acetone at the temperature range from 283.15 K to 323.15 K

	a	b	c	10^4RMSD
0.0000	−430.4484	15632.2231	65.7431	6.8794
0.1229	−379.3075	13261.8645	58.1433	8.3045
0.2396	−347.1361	11824.5169	53.3203	8.4405
0.3508	−338.2044	11415.6200	51.9650	5.3076
0.4567	−351.7632	12027.2080	53.9520	2.5818
0.5577	−363.1927	12528.6810	55.6254	1.3936
0.6541	−375.7840	13081.5003	57.4666	0.0951
0.7463	−400.4545	14177.6314	61.1014	1.9516
0.8345	−430.4721	15509.1587	65.5292	1.9915
0.9190	−510.2020	18977.2258	77.4120	1.8838
1.0000	−552.3998	21061.0493	83.5392	0.0407

where N is the number of experimental points, $x_{1,j}^{calc}$ is the solubility calculated from Eq. (6) and $x_{1,j}$ is the experimental value of solubility. It can be seen from Table 2 that the experimental and correlated results are in good agreement.

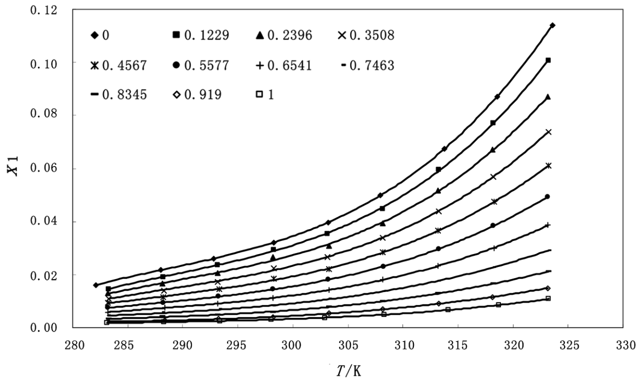

Fig. 2. Solubility of 4-(3,4-dichlorophenyl)-1-tetralone x_1 in different solvent composition.

CONCLUSIONS

The following conclusions are drawn from this work:

1. The solubility of 4-(3,4-dichlorophenyl)-1-tetralone in the ethanol and acetone mixture increases with increasing temperature (see Fig. 2).

2. At a given temperature, the solubility of 4-(3,4-dichlorophenyl)-1-tetralone decreases with increasing concentration of ethanol in the solvent mixtures. Therefore, the solubility in pure ethanol is the lowest.

3. These experimental data can be regressed by Eq. (6) for each solvent mixture. The experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of 4-(3,4-dichlorophenyl)-1-tetralone.

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