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SHORT COMMUNICATION

Solubility of 4-(3,4-dichlorophenyl)-1-tetralone in eleven alcohols with the temperature range from 283 K to 323 K

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Abstract−The solubility of 4-(3,4-dichlorophenyl)-1-tetralone in eleven alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 2-propanol, 2-butanol, 2-pentanol, 1,2-propanediol, 1,3-propanediol) was measured by using a laser technique with a temperature range from 283 K to 323 K, and at atmospheric pressure. For mono n-alcohols, the solubility is the lowest in methanol, increasing with the carbon chain of the alcohols. 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, Alcohols

INTRODUCTION

4-(3,4-Dichlorophenyl)-1-tetralone ($C_{16}H_{12}Cl_2O$, molecular weight 291.17, CAS Registry No. 79560-19-3) is a kind of white or almost white crystalline powder. 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, hence some organic solvents, such as ethanol, acetone, toluene, THF and so on, are employed in the production of sertraline hydrochloride [2]. To determine proper solvents and to design an optimized production process, it is necessary to know the solubility of 4-(3,4-dichlorophenyl)-1-tetralone in different solvents. However, from a review of the literature, it was found that no experimental solubility data were available. In this paper, the solubility of 4-(3,4-dichlorophenyl)-1-tetralone in eleven alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 2-propanol, 2-butanol, 2-pentanol, 1,2-propanediol, 1,3-propanediol) was experimentally determined in the temperature range from 283 K to 323 K. The method employed in this work was classed as a synthetic method, which was much faster and functioned 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. Its mass fraction purity determined by HPLC was higher than 99.2%. All alcohols were analytical research grade reagent from Beijing Chemical Reagent Co.

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 [5] and described briefly here. A 100 and 250 mL jacked vessel were 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 required 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 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 the laser intensity reached maximum. Then, additional solute of known mass {about (1 to 5) mg} was introduced into the vessel. This procedure was repeated until the penetrated laser intensity could not return maximum, or in other words, 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):

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

where m_1 and m_2, represent the mass of the solute and solvent, and M_1 and M_2, are the molecular weight of the solute and the solvent, respectively.

RESULTS AND DISCUSSION

The solubilities of 4-(3,4-dichlorophenyl)-1-tetralone in eleven

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Table 1. Mole fraction solubility (x_1) of 4-(3,4-dichlorophenyl)-1-tetralone in selected alcohols with a temperature range from 283 K to 323 K

T/K	$10^3\,x_1$	$10^3\,x_1^{calc}$	$10^3\,(x_1-x_1^{calc})$	T/K	$10^3\,x_1$	$10^3\,x_1^{calc}$	$10^3\,(x_1-x_1^{calc})$
			methanol				
283.06	1.0704	1.0555	0.0149	308.56	3.7213	3.6914	0.0299
288.28	1.4085	1.4286	−0.0201	313.53	4.4626	4.4372	0.0254
293.42	1.8587	1.8775	−0.0188	319.04	5.3331	5.3349	−0.0018
298.04	2.3506	2.3534	−0.0028	323.25	6.0221	6.0606	−0.0385
302.77	2.9283	2.9121	0.0162				
			ethanol				
283.12	1.7150	1.7309	−0.0159	308.32	4.9024	4.9122	−0.0098
288.27	2.0993	2.0659	0.0334	314.17	6.6686	6.6192	0.0494
293.38	2.5236	2.5116	0.0012	318.74	8.5181	8.4591	0.0590
298.04	3.0282	3.0495	−0.0213	323.26	10.8252	10.8881	−0.0629
302.93	3.7593	3.7954	−0.0361				
			1-propanol				
283.16	2.2354	2.2488	−0.0134	308.26	7.5614	7.5637	−0.0023
288.27	2.8670	2.8346	0.0324	313.17	9.8341	9.7764	0.0577
293.19	3.5768	3.5712	0.0056	318.24	12.8832	12.8110	0.0722
298.18	4.5153	4.5478	−0.0325	323.16	16.6396	16.7335	−0.0939
303.22	5.8059	5.8461	−0.0402				
			1-butanol				
283.18	2.7694	2.8359	−0.0665	308.18	9.3759	9.4724	−0.0965
288.16	3.6329	3.5304	0.1025	313.20	12.4093	12.4104	−0.0011
293.29	4.5485	4.4772	0.0713	318.26	16.5296	16.4220	0.1076
298.19	5.6477	5.6763	−0.0286	323.19	21.7706	21.7245	0.0461
303.32	7.2451	7.3506	−0.1055				
			1-pentanol				
283.17	5.3489	5.4167	−0.0678	308.21	14.1917	14.4309	−0.2392
288.19	6.4774	6.4960	−0.0186	313.26	17.6770	17.9288	−0.2518
293.16	8.0484	7.8380	0.2104	318.27	22.3175	22.3534	−0.0359
298.18	9.6768	9.5448	0.1320	323.20	28.3105	27.9025	0.4080
303.19	11.6270	11.6974	−0.0704				
			1-hexanol				
283.18	4.4282	4.3946	0.0336	308.21	14.1869	14.0726	0.1143
288.19	5.4358	5.4363	−0.0005	313.29	18.5473	18.3097	0.2376
293.20	6.7326	6.7989	−0.0663	318.17	23.9076	23.7437	0.1639
298.26	8.5238	8.6099	−0.0861	323.16	30.7557	31.1757	−0.4200
303.16	10.8977	10.9205	−0.0228				
			2-propanol				
283.38	1.2751	1.2610	0.0141	308.46	4.9575	4.9075	0.0500
288.33	1.6340	1.6401	−0.0061	313.26	6.4917	6.4049	0.0868
293.07	2.0880	2.1154	−0.0274	318.54	8.6440	8.5987	0.0453
298.33	2.7840	2.8135	−0.0295	323.21	11.0110	11.1712	−0.1602
303.36	3.7040	3.7048	−0.0008				

alcohols at different temperatures are shown in Table 1 and Fig. 1.

The solubility of a solid in a liquid may be expressed in a very general manner by Eq. (2):

$$\ln x_1 = -\frac{\Delta H_{f,1}}{\mathrm{R}T_{f,1}}\left(\frac{T_{f,1}}{T}-1\right) - \frac{\Delta \mathrm{C}_{pf,1}}{\mathrm{R}}\left(\frac{T_{f,1}}{T}-1\right) + \frac{\Delta \mathrm{C}_{pf,1}}{\mathrm{R}}\ln\frac{T_{f,1}}{T} - \ln\gamma_1 \qquad (2)$$

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 Eq. (3):

$$\ln\gamma_1 = A + \frac{B}{T} \qquad (3)$$

where A and B stand for empirical constants. Introducing γ_1 from

Table 1. Continued

T/K	$10^3\,x_1$	$10^3\,x_1^{calc}$	$10^3\,(x_1-x_1^{calc})$	T/K	$10^3\,x_1$	$10^3\,x_1^{calc}$	$10^3\,(x_1-x_1^{calc})$
			2-butanol				
283.19	1.8285	1.8427	−0.0142	308.16	7.5729	7.5727	0.0002
288.26	2.4810	2.4431	0.0379	313.18	10.1930	10.1202	0.0728
293.18	3.2274	3.2210	0.0064	318.22	13.6477	13.5584	0.0893
298.20	4.2435	4.2808	−0.0373	323.17	17.9827	18.0899	−0.1072
303.29	5.6801	5.7244	−0.0443				
			2-pentanol				
283.17	3.4567	3.4712	−0.0145	308.28	11.0828	11.0547	0.0281
288.21	4.2912	4.2343	0.0569	313.22	14.6736	14.5050	0.1686
293.26	5.2578	5.2627	−0.0049	318.21	19.4983	19.3185	0.1798
298.18	6.5369	6.6115	−0.0746	323.19	25.7266	26.0075	−0.2809
303.27	8.4316	8.5044	−0.0728				
			1,2-propanediol				
283.27	0.7315	0.7766	−0.0451	308.20	2.2737	2.3569	−0.0832
288.19	1.0308	0.9790	0.0518	313.19	2.8062	2.8923	−0.0861
293.18	1.2939	1.2300	0.0639	318.26	3.5271	3.5421	−0.0150
298.32	1.5677	1.5459	0.0218	323.22	4.4510	4.2972	0.1538
303.17	1.8706	1.9068	−0.0362				
			1,3-propanediol				
283.16	0.3068	0.2827	283.16	308.27	1.5396	1.4808	0.0588
288.17	0.3918	0.4269	288.17	313.20	1.8908	1.8389	0.0519
293.28	0.5878	0.6217	293.28	318.18	2.2226	2.2184	0.0042
298.19	0.8547	0.8571	298.19	323.20	2.5078	2.6012	−0.0934
303.22	1.1822	1.1466	303.22				

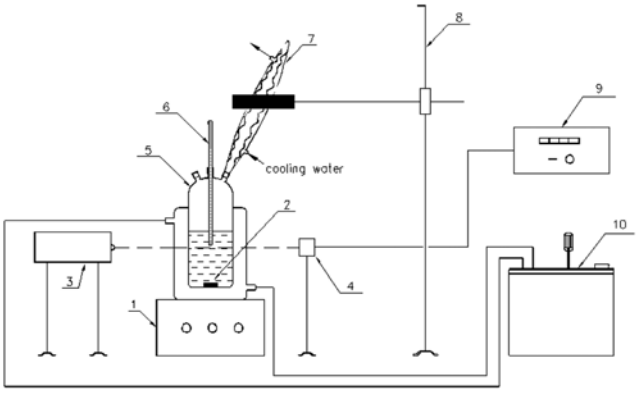

Fig. 1. Schematic setup for the solubility measure.

1. Magnetic stirrer
2. Stir bar
3. Laser generator
4. Photoelectric converter
5. Dissolution vessel
6. Thermometer
7. Condenser
8. A ring stand and clamp
9. Digital display
10. Thermostat

Eq. (3) into Eq. (2) and subsequent rearrangements results in Eq. (4):

$$\ln x_1=\left[\frac{\Delta H_{f,1}}{\mathrm{R}T_{f,1}}+\frac{\Delta \mathrm{C}_{pf,1}}{\mathrm{R}}(1+\ln T_{f,1})-A\right]-\left[B+\left(\frac{\Delta H_{f,1}}{\mathrm{R}T_{f,1}}+\frac{\Delta \mathrm{C}_{pf,1}}{\mathrm{R}}\right)T_{f,1}\right]\frac{1}{T}-\frac{\Delta \mathrm{C}_{pf,1}}{\mathrm{R}}\ln T \quad (4)$$

Eq. (4) can be written as

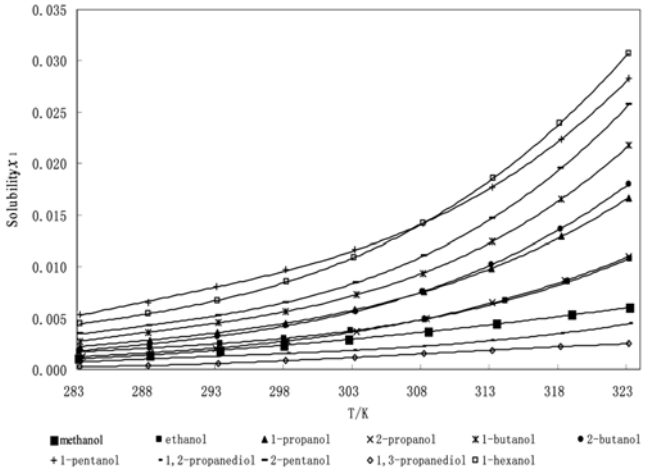

Fig. 2. Solubility of 4-(3,4-dichlorophenyl)-1-tetralone in all selected alcohols.

$$\ln x_1=a+\frac{b}{T}+c\ln T \quad (5)$$

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

The solubility data are correlated with Eq. (5). The difference between experimental and calculated 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. The RMSD is defined as the following:

Table 2. Parameters of equation 5 for 4-(3,4-dichlorophenyl)-1-tetralone in selected alcohols with a temperature range from 283 K to 323 K

	a	*b*	*c*	10^5 *RMSD*
Methanol	311.3838	−17674.4552	−45.3086	2.3115
Ethanol	−552.3998	21061.0493	83.5392	4.0686
1-Propanol	−351.6859	11699.0190	53.8916	5.1597
2-Propanol	−263.4346	7346.4153	40.8789	7.0363
1-Butanol	−419.9794	14730.0576	64.1325	8.2898
2-Butanol	−266.1203	7302.1762	41.4512	6.1032
1-Pentanol	−312.3093	10675.9999	47.7129	21.2121
1,2-Propanediol	−25.2014	−2484.9025	4.7487	7.8103
2-Pentanol	−549.6851	20623.0596	83.4553	13.9098
1,3-Propanediol	671.2997	−34860.7432	−98.5399	4.8897
1-Hexanol	−401.5110	14062.8089	61.3564	18.9156

$$RMSD = \left[\frac{\sum_{j=1}^{N} (x_{1,j} - x_{1,j}^{calc})^2}{N-1} \right]^{1/2} \quad (6)$$

where N is the number of experimental points; $x_{1,j}^{calc}$ is the solubility calculated from Eq. (5); and $x_{1,j}$ is the experimental value of solubility.

From Table 1, Table 2, and Fig. 1, the following conclusions can be drawn: (1) The solubility of 4-(3,4-dichlorophenyl)-1-tetralone in all selected alcohols increases with increase of temperature. (2) For mono n-alcohols, the solubility of 4-(3,4-dichlorophenyl)-1-tetralone is the lowest in methanol, increasing with the carbon chain of the alcohols. (3) These experimental data can be regressed by Eq. (5) for each selected alcohol. 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.

CONCLUSIONS

The solubility of 4-(3,4-dichlorophenyl)-1-tetralone in all selected alcohols increases with increase of temperature. The solubility of 4-(3,4-dichlorophenyl)-1-tetralone in mono n-alcohols is the lowest in methanol, increasing with the carbon chain of the alcohols. These experimental data can be regressed by Eq. (5) for each selected alcohol. The calculated solubility shows good agreement with the experimental values. 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.

REFERENCES

1. V. Krisztina, F. Tamás, F. János, F. Irén and L. Sándor, *Organic Process & Development*, **6**, 82 (2002).
2. P. T. Geraldine, M. P. David and C. C. Juan, *Organic Process & Development*, **8**, 385 (2004).
3. Y. Jaesook and L. B. Stephen, *J. Org. Chem.*, **65**, 767 (2000).
4. G. T. Heffter and R. P. T. Tomkins, John Wiley, Chichester, 260 (2003).
5. K. S. Kim, D. Demberelnyamba, B. K. Shin, S.-H. Yeon, S. Choi, J.-H. Cha, H. Lee, C.-S. Lee and J.-J. Shim, *Korean J. Chem. Eng.*, **23**, 113 (2006).
6. S. Wang and D. X. Chen, *Korean J. Chem. Eng.*, **23**, 1034 (2006).
7. G. B. Ren, J. K. Wang, Q. X. Yin and M. J. Zhang, *J. Chem. Eng. Data*, **49**, 1671 (2004).
8. S. Wang, J. K. Wang, Q. X. Yin and Y. L. Wang, *Chinese Optics Letters*, **3**, 149 (2005).
9. S. Wang, J. K. Wang and Q. X. Yin, *Ind. Eng. Chem. Res.*, **44**, 3783 (2005).
10. X. N. Li, Q. X. Yin, W. Chen and J. K. Wang, *J. Chem. Eng. Data*, **51**, 127 (2006).
11. H. X. Hao, J. K. Wang and Y. L Wang, *J. Chem. Eng. Data*, **49**, 1697 (2004).
12. D. Q. Li, D. Z. Liu and F. A. Wang, *J. Chem. Eng. Data*, **46**, 234 (2001).