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Articles

Solubility of Organic Systems Containing 1,4-Dioxan-2-one

Sung-Il Kim,[†] Chul-Ung Kim,[†,*] and So-Jin Park[‡]

Chemical Process and Engineering Center, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon, 305-600 Korea, and Department of Chemical Engineering, Chungnam National University, Yuseong, Daejeon, 305-764 Korea

The mole fraction solubility of 1,4-dioxan-2-one (x_1) in tetrahydrofuran, acetone, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol were measured over the temperature range from 263.05 K to 288.45 K. The solubility of 1,4-dioxan-2-one in alcohols increases with increasing polarity of the solvent. The results were fitted by the exponential equation. The result of the solubility was well-correlated by the empirical equations: $x_1 = \alpha e^{\beta}(T/\mathrm{K})$ where T is absolute temperature and α and β are parameters.

Introduction

The present paper is a contribution to our ongoing research on the thermodynamic properties of binary mixtures containing 1,4-dioxan-2-one (*p*-dioxanone), a monomer of biodegradable polymer.[1−3]

An exceptionally high purity over 99.9 % of the 1,4-dioxan-2-one monomer is required for polymerization to a high molecular weight polymer. Solution crystallization has been applied to the purification of this compound due to the property of a thermally unstable ether group. For the effective removal of impurity and the kinetic of crystallization such as nucleation and crystal growth, the solubility and the density of 1,4-dioxan-2-one in solution must be known, and selecting the proper solvent is very important.[1−4] However, there appears to be few previous measurements on the solubility and density for the system including 1,4-dioxan-2-one in solvent.

In this work, the measurement has been conducted on the solubility of 1,4-dioxan-2-one in various solvents such as tetrahydrofuran, acetone, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol over the temperature range from 263.05 K to 293.05 K, which are adequate operating conditions of solution crystallization of 1,4-dioxan-2-one.

Experimental Section

Materials. 1,4-Dioxan-2-one (solid below 301.41 K) was prepared and purified in our pilot plant according to procedures in refs 2 and 3. The materials were analyzed by flame ionization detection gas chromatograph (FID, Hewlett-Packard 5890 series II) equipped with capillary columns (BP20 1.0 UM, SGE). The mass fraction purity was >99.9 %. The solvents were from commercial sources (Aldrich, Merck) and analytical reagent grade with a minimum purity >99 %. Before their use, all compounds were stored over molecular sieves to avoid contamination with water. For 1,4-dioxan-2-one, the enthalpy of fusion ($\Delta_{\mathrm{fus}}H_1$) and melting point were determined by differential scanning calorimeter (DSC 2910; TA Instruments, USA) with an uncertainty of ± 0.05 kJ·mol^{-1} and are compared with the literature values in Table 1.

Table 1. Comparison of Experimental Melting Point and Enthalpy of Fusion with Literature Values

melting point/K		enthalpy of fusion/kJ·mol^{-1}	
exptl	lit[5]	exptl	lit[5]
301.41[a]	301.69[b]	15.70[a]	16.14[c]

[a] Determined by differential scanning calorimeter. [b] Determined using the dependence of thermodynamically equilibrium triple points on the fractional content of melt. [c] Using a method of continuous energy supply.

Measurement of Solubility. The mixtures were prepared by mass using a Mettler AG 204 balance with an uncertainty of ± 0.0001 g. The estimated uncertainty in the mole fraction is better than $\pm 2 \times 10^{-4}$. The solubility of 1,4-dioxan-2-one in the various solvents (tetrahydrofuran, acetone, methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol) were measured using a polythermal method described in detail previously.[6−8] The equilibrium cell, a cylindrical glass vessel (50 mm inside diameter, 120 mm long), was placed by ground-glass joint in a triple-jacketed vessel. The outer jacket was evacuated, and either heated or cooled fluid from a thermostated bath could be circulated through the middle jacket. An ethylene glycol + water solution was thermostated and controlled by a thermoelectric Eurotherm 808 PID controller with ± 0.1 K uncertainty. The cell had a perforated rubber stopper through which a copper−constantan thermocouple was insertted. The contents were stirred with a magnetic spin bar. The cell was tightly sealed to protect the system from dust and moisture condensation. Mixtures of solute and solvent were cooled in the bath until an abundant amount of crystal was formed and then heated very slowly at less than 0.001 K·min^{-1} near the equilibrium temperature. The crystal disappearance temperature, detected visually, was measured with a calibrated thermocouple connected to a recorder (Yokogawa, 180 micro R). The thermocouples were calibrated with a calibrated thermometer from Fisher Scientific (no. 15-078-7) with an uncertainty of ± 0.05 K. The uncertainty of the thermocouple measurements is believed to be ± 0.1 K. Some of the experiments were conducted in triplicate to check the reproducibility. The saturation temperature for a given mixture was uncertainty within ± 0.1 K.

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[*] Corresponding author. E-mail: cukim@krict.re.kr.
[†] Korea Research Institute of Chemical Technology.
[‡] Chungnam National University.

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Table 2. Experimental Solubilities of 1,4-Dioxan-2-one (x_1) in Various Solvents

acetone		tetrahydrofuran		methanol		ethanol		1-propanol		1-butanol		1-pentanol	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.2766	263.05	0.1531	263.25	0.0557	263.15	0.0145	263.45	0.0055	263.15	0.0029	263.15	0.0012	263.15
0.3114	265.55	0.1752	265.55	0.0693	265.75	0.0215	265.65	0.0086	265.55	0.0043	265.75	0.0017	265.75
0.3326	268.15	0.2000	268.15	0.0864	268.05	0.0272	268.15	0.0120	268.45	0.0058	268.05	0.0029	268.25
0.3608	270.55	0.2311	271.05	0.1084	270.95	0.0390	270.95	0.0173	270.65	0.0091	270.55	0.0040	270.85
0.4019	273.15	0.2683	273.45	0.1400	273.45	0.0492	273.15	0.0233	273.15	0.0134	273.45	0.0052	273.15
0.4395	275.65	0.2958	275.55	0.1876	275.75	0.0660	275.75	0.0345	275.65	0.0227	275.95	0.0091	275.95
0.4859	278.45	0.3437	278.15	0.2394	278.05	0.1016	278.25	0.0468	278.45	0.0287	278.15	0.0142	278.25
0.5325	280.75	0.3905	281.05	0.3166	280.85	0.1501	280.75	0.0761	280.65	0.0536	280.55	0.0219	280.75
0.5778	283.25	0.4561	283.15	0.4022	283.15	0.2101	283.15	0.1131	283.15	0.0681	283.25	0.0291	283.05
0.6371	285.55	0.5264	286.05	0.5067	285.65	0.3119	285.75	0.1757	285.95	0.1137	285.95	0.0466	285.65
0.6813	288.45	0.6017	288.35	0.6212	288.45	0.4094	288.35	0.2376	288.05	0.1529	288.15	0.0631	288.15

Table 3. Values of Parameters for Equation 1 in Various Solvents

system	α	β/K^{-1}	RSD	AAD
acetone	2.1840×10^{-5}	0.0359	0.017	0.004
tetrahydrofuran	9.8757×10^{-8}	0.0541	0.017	0.005
methanol	2.6211×10^{-13}	0.0989	0.040	0.010
ethanol	5.7652×10^{-18}	0.1346	0.065	0.005
1-propanol	4.1658×10^{-20}	0.1498	0.062	0.003
1-butanol	9.4138×10^{-22}	0.1616	0.065	0.002
1-pentanol	3.5402×10^{-22}	0.1620	0.062	0.001

Results and Discussion

Solubility. The solubility of 1,4-dioxan-2-one in various solvents such as tetrahydrofuran, acetone, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol were measured over the temperature range from 263.05 K to 288.45 K, and the values are listed in Table 2 and plotted in Figure 1. The solubilities of 1,4-dioxan-2-one increase with an increase in the temperature and decrease with an increase in the number of carbon atoms in alcohols. This means that the solubility of 1,4-dioxan-2-one in alcohols increases with increasing polarity of the solvents. In different types of solvents, the temperature dependence of the solubility of 1,4-dioxan-2-one was in the order of acetone > tetrahydrofuran > alcohols, which depended on the difference between interactions of solute and solvent.

It was found that exponential temperature dependence, as shown in Figure 1, permitted a linear interpolation. Thus, the mole fraction solubility x_1 of 1,4-dioxan-2-one was analyzed using the following equation:[6]

$$x_1 = \alpha e^{\beta}(T/\mathrm{K}) \tag{1}$$

where T is the absolute temperature and α and β are parameters. The exponential expression describes satisfactorily the temperature dependence of the solubility, within the temperature range studied. The binary parameters for eq 1 with the relative standard deviation (RSD) and the absolute average deviation (AAD) are given in Table 3. For all studied systems, the obtained RSD and AAD are smaller than 0.065 and 0.004, respectively.

The RSD is defined by

$$\mathrm{RSD} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(\frac{x_{1,i}(\mathrm{calc}) - x_{1,i}}{x_{1,i}}\right)^2\right]^{1/2} \tag{2}$$

and the AAD is defined by

$$\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N}|(x_{1,i}(\mathrm{calc}) - x_{1,i})| \tag{3}$$

where N is the number of data points.

Solubility data can be used to estimate the activity coefficient through the equilibrium relationship. If no solid−solid transition

Table 4. Activity Coefficient of 1,4-Dioxan-2-one in Various Solvents

acetone			tetrahydrofuran			methanol			ethanol			1-propanol			1-butanol			1-pentanol		
T/K	x_1^{L}	γ_1^{L}	T/K	x_1^{L}	γ_1^{L}	T/K	x_1^{L}	γ_1^{L}	T/K	x_1^{L}	γ_1^{L}	T/K	x_1^{L}	γ_1^{L}	T/K	x_1^{L}	γ_1^{L}	T/K	x_1^{L}	γ_1^{L}
263.05	0.2758	1.45	263.25	0.1513	2.67	263.15	0.0526	7.65	263.45	0.0145	27.96	263.15	0.0055	73.12	263.15	0.0028	143.63	263.15	0.0012	335.15
265.55	0.3016	1.42	265.55	0.1713	2.51	265.75	0.0681	6.34	265.65	0.0195	22.07	265.55	0.0079	54.32	265.75	0.0042	102.72	265.75	0.0018	239.68
268.15	0.3312	1.39	268.15	0.1972	2.33	268.05	0.0855	5.36	268.15	0.0273	16.84	268.45	0.0121	38.30	268.05	0.0061	75.17	268.25	0.0026	177.29
270.55	0.3610	1.36	271.05	0.2307	2.15	270.95	0.1138	4.35	270.95	0.0398	12.42	270.65	0.0169	29.03	270.55	0.0092	53.19	270.85	0.0040	123.30
273.15	0.3963	1.32	273.45	0.2626	2.01	273.45	0.1458	3.61	273.15	0.0535	9.78	273.15	0.0246	21.26	273.45	0.0146	36.09	273.15	0.0058	90.17
275.65	0.4335	1.28	275.55	0.2942	1.89	275.75	0.1830	3.05	275.75	0.0759	7.36	275.65	0.0357	15.60	275.95	0.0219	25.62	275.95	0.0092	60.98
278.45	0.4793	1.25	278.15	0.3387	1.75	278.05	0.2297	2.57	278.25	0.1062	5.59	278.45	0.0543	10.99	278.15	0.0313	18.92	278.25	0.0134	44.30
280.75	0.5206	1.21	281.05	0.3962	1.60	280.85	0.3030	2.09	280.75	0.1487	4.24	280.65	0.0755	8.33	280.55	0.0461	13.61	280.75	0.0200	31.53
283.25	0.5695	1.17	283.15	0.4439	1.50	283.15	0.3804	1.76	283.15	0.2054	3.25	283.15	0.1098	6.08	283.25	0.0713	9.39	283.05	0.0291	22.89
288.55	0.6185	1.14	286.05	0.5193	1.38	285.65	0.48716	1.45	285.75	0.2915	2.43	285.95	0.1671	4.27	285.95	0.1102	6.47	285.65	0.0443	15.98
288.45	0.6863	1.10	288.35	0.5881	1.28	288.45	0.6426	1.17	288.35	0.4136	1.82	288.05	0.2288	3.27	288.15	0.1573	4.77	288.15	0.0664	11.29

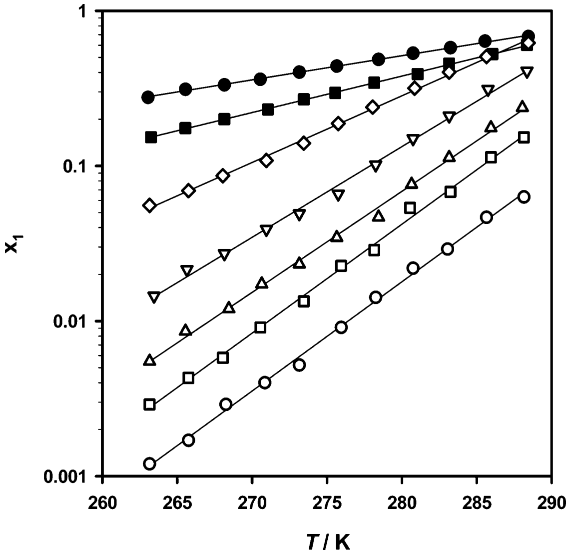

Figure 1. Mole fraction solubility of 1,4-dioxan-2-one (1) with various solvents: ●, acetone; ■, tetrahydrofuran; ◇, methanol; ▽, ethanol; ○, 1-propanol; △, 1-butanol; □. 1-pentanol.

occurs in the temperature range, the following equation can be used to calculate the solid−liquid-phase equilibria:[9,10]

$$\ln x_1^{\mathrm{L}}\gamma_1^{\mathrm{L}} = -\frac{\Delta_{\mathrm{fus}}H_1}{R}\left[\frac{1}{T} - \frac{1}{T_{\mathrm{fus},1}}\right] \tag{4}$$

where x_1^{L} is the mole fraction of component 1 (1,4-dioxan-2-one) in the liquid phase, γ_1^{L} is the activity coefficient of component 1 in the liquid phase, $\Delta_{\mathrm{fus}}H_1$ is the molar enthalpy of fusion of component 1, $T_{\mathrm{fus},1}$ is the melting temperature of component 1, T is the absolute temperature of the mixture, and R is the universal gas constant. The activity coefficients γ_1^{L} can be calculated using eq 4 from experimentally determined solution composition x_1^{L} and temperature T.

Table 4 gives mole fractions, equilibrium temperature, and activity coefficients. Table 4 shows that, in nearly all the cases, positive deviation from ideal solution ($\gamma_1^{\mathrm{L}} > 1$) is encountered in the systems showed.

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