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Solubility of 1,3,5-Trioxane in Methanol, Ethanol, and 2-Propanol

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The solubility of 1,3,5-trioxane in methanol, ethanol, and 2-propanol from (293 to 328) K has been measured. The solubility results were well correlated by the nonrandom two-liquid equation.

Introduction

1,3,5-Trioxane is a trimer of formaldehyde, and because of the wide application of formaldehyde and its polymers in producing synthetic resins and many of industrial polymers, it has special importance for many years.[1−3]

Because of the thermal instability of formaldehyde polymers, they have limited applications. 1,3,5-Trioxane has good thermal stability and is used as a source for formaldehyde production. This compound can be obtained by distillation of paraformaldehyde or from concentrated solutions of formaldehyde in the presence of a nonvolatile acid as a catalyst by extraction using solvents such as alcohols, benzene, dichloroethane, and water. Therefore, it is important to have thermodynamic data for the solubility of 1,3,5-trioxane in different solvents.[4,5]

In the present study, the solubility of 1,3,5-trioxane in methanol, ethanol, and 2-propanol at various temperatures was determined, where the concentrations were measured by a gas−liquid chromatography (GLC) method. The experimental results were correlated by using the nonrandom two-liquid (NRTL) activity coefficient model.

Experimental Section

A. Sample Preparation. Reagents were pure-grade methanol, ethanol, 1-propanol, and 2-propanol by Merk and 1,3,5-trioxane by Riedel Haien. An excess amount of 1,3,5-trioxane was added to the solvents in a specially designed sealed dual-wall flask. Between the outer and inner walls of the flask, water at constant temperature was circulated. The temperature of the circulating water was controlled by a thermostat within ±0.1 K. The solution was constantly stirred using a magnet stirrer. After attaining equilibrium, the stirrer was turned off to let the solution settle for 2 h. Then the upper portion was taken and poured into a 50-mL volumetric flask. For preparing the solutions for GLC analysis, for methanol and 2-propanol, as solvents, 4 mL of 1-propanol was added, and for ethanol, 4 mL of isobutyl alcohol as an internal standard was added to the solutions. Then the solutions were diluted to 50 mL volume with double-distilled water.

B. Sample Analysis. A Perkin-Elmer 8500 GLC instrument coupled with a flame ionization detector (FID) was used for analysis of samples and detecting the composition of stock solutions for (1,3,5-trioxane + methanol), (1,3,5-trioxane + ethanol), and (1,3,5-trioxane + 2-propanol) mixtures. The GLC instrument was calibrated by using the standard solutions in the appropriate concentration range. To do this, known amounts of 1,3,5-trioxane and solvent (0.1 mg precision by mass) were added to the 50-mL volumetric flasks, and after adding 4 mL of the internal standard (1-propanol for 1,3,5-trixane + methanol and 1,3,5-trioxane + 2-propanol mixtures and isobutyl alcohol for the 1,3,5-trioxane + ethanol mixture), they were diluted to 50 mL volume by adding double-distilled water. Double-distilled water was used because the FID detector was insensitive to water and prevented possible interferences in the curves for solvent and sample components. After preparing the standard for each of the mixtures, the composition of the appropriate stock solution was determined by using the following procedures.

C. Composition Determining. At first, the standard solutions were injected to the GLC instrument, and the area under the curve for each component was determined.[6] By use of these results, the calibration curves were obtained for each solution, which was used to determine the composition of the injected stock samples.[7−8] The solubilities based on the calibration curves are presented in the Table 3. The injection of stock samples was done immediately after the standard solutions. The operating condition for GLC instrument is given in Table 1.

Results and Discussion

The measured solubilities for 1,3,5-trioxane in the solvents at various temperatures are presented in Table 2. In this table, the solubilities of 1,3,5-trioxane in methanol measured by Brandani et al.[1] are also presented. Utilizing the internal standard method for analyzing the GLC results is quite reliable and precise to ±3%.[8] Each composition measurement was repeated five times, and the results

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Table 1. Operating Conditions for the GLC Instrument

column	6% Silar 10C sorb WHP 100−200 mesh
detector temperature	180 °C
injector temperature	180 °C
oven temperature	$65\ ^\circ\mathrm{C}\ (1\mathrm{min}) \xrightarrow{20\ ^\circ\mathrm{C/min}} 90\ ^\circ\mathrm{C} \xrightarrow{25\ ^\circ\mathrm{C/min}} 105\ ^\circ\mathrm{C}$
carrier gas	nitrogen
flow rate	30 mL/min

Table 2. Mole Fraction Solubility, *x*, of 1,3,5-Trioxane in the Three Solvents at Various Temperatures

		methanol		ethanol		2-propanol	
T/K	x	T/K	x^a	T/K	x	T/K	x
293.5	0.1188	293.45	0.1115	294.3	0.1212	297.3	0.1204
298.3	0.1745	298.25	0.1690	298.4	0.1534	303.2	0.1866
303.1	0.2589	303.15	0.2505	303.2	0.2081	306.2	0.2359
308.2	0.4175	308.20	0.4020	308.2	0.3278	308.2	0.2859
313.1	0.5874	313.10	0.5745	313.1	0.4780	313.1	0.4490
318.1	0.7139	318.05	0.7055	318.1	0.6573	318.1	0.6382
323.1	0.8214	323.05	0.8140	323.1	0.8025	323.1	0.7838
328.2	0.9122	328.25	0.9060	328.3	0.9379	328.3	0.8962

[a] Work of Brandani, ref 1.

Table 3. Parameters of the NRTL Activity Coefficient Model and the Average Absolute Deviation Percent (AAD%) for Solubility of 1,3,5-Trioxane in Solvents

solvents	a	b	c	AAD%[a]
methanol	1.3756	0.4486	0.6031	0.32
ethanol	1.2712	0.6511	0.5533	0.50
2-propanol	1.3309	0.8270	0.6362	0.19

$$*\mathrm{AAD\%} = \frac{1}{N}\sum_{K=1}^{N}\frac{|x_{\mathrm{correlated}} - x_{\mathrm{experimental}}|_k}{x_{\mathrm{experimental},k}} \times 100$$

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were reproducible to the accuracy within ±0.0005 mole fraction.

The measured mole fraction solubility x_2 of 1,3,5-trioxane (2) in solvent (1) as presented in Table 3 were correlated by the following equation[9]

$$\ln(\gamma_2 x_2) = -\frac{\Delta_{\mathrm{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m}}}\right) \tag{1}$$

where γ_2, the activity coefficient of 1,3,5-trioxane, can be evaluated by various activity coefficient models.[9] In this work, the NRTL model as presented by the following equation was used[9−11]

$$\ln(\gamma_2) = x_1^2\left[a\left(\frac{\exp(-ac)}{x_2 + x_1\exp(-ac)}\right)^2 + b\left(\frac{\exp(-bc)}{x_1 + x_2\exp(-bc)}\right)^2\right] \tag{2}$$

The melting point T_{m} and the enthalpy of fusion $\Delta_{\mathrm{fus}}H$ of 1,3,5-trioxane are 333.44 K and 15105 J/mol, respectively.[10]

The optimal NRTL parameters, a, b, and c, in eq 2 were calculated from the regression of the objective function $\sum_i[\ln(\gamma_2) - \ln(\gamma_2)_{\mathrm{NRTL}}]^2$, where $(\gamma_2)_{\mathrm{NRTL}}$ was evaluated from eq 2 for the experimental value of x_2. Calculations of the correlated mole fraction solubility of 1,3,5-trioxane in methanol, ethanol, and 2-propanol were performed with the replacement of γ_2 in eq 1 by $(\gamma_2)_{\mathrm{NRTL}}$ using the optimal parameters. The correlated mole fraction solubility of 1,3,5-trioxane in methanol, ethanol, and 2-propanol were compared with the experimental results in Figure 1. The parameters of the NRTL model and the average absolute deviations (*AAD%*) are given in Table 3.

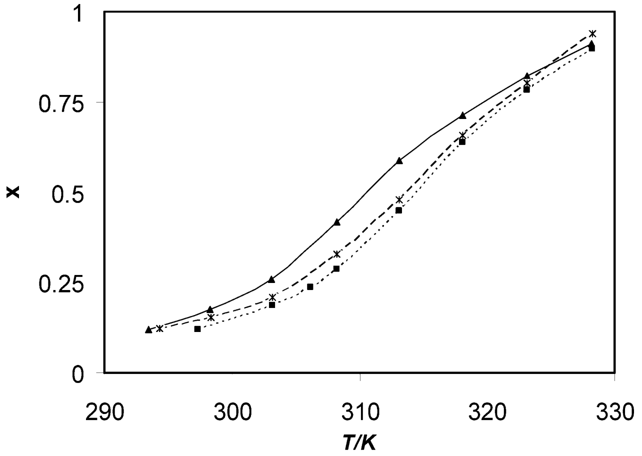

Figure 1. The mole fraction solubility, x, of 1,3,5-trioxane in ▲, methanol; *, ethanol; ■, 2-propanol at various temperatures. Lines represent the correlated results by NRTL model.

Conclusions

GLC measurements were used to determine the solubility of 1,3,5-trioxane in methanol, ethanol, and 2-propanol. The solubility data were used to evaluate the NRTL parameters. The results indicated that the NRTL activity coefficient model was able to correlate the solubility of 1,3,5-trioxane in the light alcohol solvents with very small and negligible errors.

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