Solubility of Thiourea in C_1 to C_6 1-Alcohols

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The solubility of thiourea in C_1 to C_6 1-alcohols was measured over the temperature range from 293.15 to 333.15 K. The results were correlated by an exponential equation.

Introduction

Thiourea is a complexing agent used in the separation of naphthenes, isoparaffins, and aromatic compounds by adductive crystallization (1-3). One method of adductive crystallization is to precipitate thiourea + hydrocarbon complexes with solvent at temperatures from 293.15 to 333.15 K. To achieve a rapid rate of adduct formation in the crystallization process, a polar solvent capable of dissolving both hydrocarbon and thiourea is required. Usually, solvents used in the process of thiourea adduction are alcohols. The solubility of thiourea in these alcohols must be known in order to interpret the kinetic data of the thiourea adduction. The results available in the literature (4) are quite scattered and in some cases appear to be unreliable. There appear to be no previous measurements on the solubility of thiourea in alcohols higher than C_3 1-alcohol. In this work, the solubility of thiourea in C_1 to C_6 1-alcohols in the temperature range from 293.15 to 333.15 K, which is the operating condition of thiourea adduction, has been measured.

Experimental Section

Thiourea was from Waco Pure Chemical Ind. Co., 99.5 mol % pure. The alcohols used in this work were from Merck, analytical reagent grade with a minimum purity of 99.9 mol %. Before use, thiourea was purified further by recrystallization. All the alcohols were used without further purification. The equilibrium cell, a cylindrical glass vessel (50-mm i.d., 120 mm long), was placed, by means of a ground-glass joint, in a the triple-jacketed vessel. The outer jacket was evacuated, and either heated or cooled water from a water bath could be circulated through the middle jacket. The water was thermostated and controlled by a thermoelectric Eurotherm 808 PID controller. The cell had a perforated rubber stopper, through which a copper–constantan thermocouple was inserted. 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 prepared by weighing pure compounds to within 1×10^{-7} kg. Mixtures of solute and solvent, cooled in the water bath until an abundant amount of crystal was formed, were heated very slowly (at less than 2 K h^{-1} near the equilibrium temperature) with continuous stirring inside a Pyrex glass cell. The crystal disappearance temperature, detected visually, was measured with a calibrated thermocouple connected to a recorder (Yokogawa, 180 Micro). Some of the solubility experiments were conducted in triplicate to check the reproducibility. The observed error in the reproducibility was less than 1.2%.

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Table 1. Refractive Index n and Density ρ at 298.15 K

| | n | | $\rho/(\text{kg m}^{-3})$ | |
solvent	obsd	lit. (6)	obsd	lit. (6)
methanol	1.3262	1.3264	786.6	786.6
ethanol	1.3589	1.3592	785.3	785.0
1-propanol	1.3832	1.3834	800.0	799.4
1-butanol	1.3972	1.3974	806.4	805.8
1-pentanol	1.4068	1.4080	811.3	810.8
1-hexanol	1.4150	1.4157	815.8	815.3

The density of the liquid solutions was determined with a 50 cm^3 pycnometer of the Gay-Lussac type. The physical properties of pure solvents are shown in Table 1. For thiourea the enthalpy of fusion, $\Delta_{fus}H = 12.552$ kJ·mol^{-1}, and the melting temperature, $T_t = 452.2$ K, were determined by differential scanning calorimetry (DSC; Shimadzu). The densities for the binary mixtures of solvents and thiourea are reported in Table 2.

Results and Discussion

The solubilities of thiourea in C_1 to C_6 1-alcohols were measured over the temperature range from 293.15 to 333.15 K. The solubility values of the thiourea in alcohols are listed in Table 3 and are plotted in Figure 1. The solubilities of thiourea decrease with an increase in the number of carbon atoms in alcohols and increase with an increase in the temperature. This means that the solubility of thiourea in alcohols increases with increasing polarity of the solvent. It was found that an exponential temperature dependence, as shown in Figure 1, permitted a linear interpolation. Thus, the solubility data were analyzed using the equation

$$s/(\text{g of solute } (100 \text{ g of solvent})^{-1}) = \alpha \exp(\beta(T/\text{K})) \quad (1)$$

where T is the absolute temperature in kelvin and α and β are constants. The linear expression describes satisfactorily the temperature dependence of the solubility, within the temperature range studied. The values of α and β in eq 1 are given in Table 4.

Data of solubility can be used to estimate the activity coefficient through the equilibrium relationship: (5)

$$\ln \gamma_1 = -\ln x_1 + \frac{\Delta_{fus}H_1}{R}\left(\frac{1}{T_{r,1}} - \frac{1}{T}\right) -$$
$$\frac{\Delta_s^{l}C_{p,1}}{R}\left(\ln\left(\frac{T_{t,1}}{T}\right) - \frac{T_{t,1}}{T} + 1\right) + \frac{\Delta_{tr}H_1}{R}\left(\frac{1}{T_{tr,1}} - \frac{1}{T}\right) \quad (2)$$

where x_1, γ_1, $\Delta_{fus}H_1$, $\Delta_s^{l}C_{p,1}$, $T_{t,1}$, and T stand for the mole

Table 2. Experimental Densities for Binary Mixtures

Thiourea (1) + Methanol (2)

	$\rho/(\text{kg m}^{-3})$					$\rho/(\text{kg m}^{-3})$			
	$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$		$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$
T/K	0.0457	0.0518	0.0585	0.0661	T/K	0.0457	0.0518	0.0585	0.0661
293.15	836.4				318.5	822.5	830.0	836.1	844.1
298.15	833.7	841.3			323.15	819.8	827.1	833.3	841.2
303.15	830.8	838.4	844.6		328.15	817.0	824.3	830.4	838.4
308.15	828.2	835.6	841.8	849.8	333.15	814.2	821.5	827.6	835.5
313.15	825.3	832.8	838.9	846.9	338.15	811.5	818.7	824.8	832.7

Thiourea (1) + Ethanol (2)

	$\rho/(\text{kg m}^{-3})$					$\rho/(\text{kg m}^{-3})$			
	$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$		$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$
T/K	0.0225	0.0253	0.0284	0.0319	T/K	0.0225	0.0253	0.0284	0.0319
293.15	800.2				318.15	784.9	787.7	790.3	791.0
298.15	797.2	800.3			323.15	781.8	784.6	787.0	787.9
303.15	794.1	797.1	799.0		328.15	778.8	781.4	783.9	784.8
308.15	791.0	794.0	796.1	797.2	333.15	775.7	778.3	780.8	781.7
313.15	788.0	790.8	792.9	794.1	338.15	772.6	775.1	777.8	779.6

Thiourea (1) + 1-Propanol (2)

	$\rho/(\text{kg m}^{-3})$					$\rho/(\text{kg m}^{-3})$			
	$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$		$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$
T/K	0.0139	0.0158	0.0179	0.0203	T/K	0.0139	0.0158	0.0179	0.0203
293.15	814.9				318.15	793.8	795.2	797.7	798.6
298.15	810.8	812.4			323.15	789.4	790.9	793.4	794.3
303.15	806.4	808.1	810.6		328.15	785.2	786.6	789.1	790.0
308.15	802.2	803.8	806.3	807.2	333.15	780.9	782.3	784.8	785.6
313.15	798.0	799.5	802.0	802.9	338.15	776.7	777.9	780.5	781.3

Thiourea (1) + 1-Butanol (2)

	$\rho/(\text{kg m}^{-3})$					$\rho/(\text{kg m}^{-3})$			
	$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$		$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$
T/K	0.0116	0.0132	0.0150	0.0171	T/K	0.0116	0.0132	0.0150	0.0171
293.15	818.7				318.15	800.2	801.2	801.8	802.4
298.15	815.0	815.8			323.15	796.5	797.6	798.1	798.7
303.15	811.3	812.2	812.7		328.15	792.8	794.0	794.5	795.1
308.15	807.5	808.5	809.1	809.7	333.15	789.1	790.4	790.8	791.4
313.15	803.9	804.8	805.4	806.0	338.15	785.4	786.7	787.2	787.8

Thiourea (1) + 1-Pentanol (2)

	$\rho/(\text{kg m}^{-3})$					$\rho/(\text{kg m}^{-3})$			
	$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$		$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$
T/K	0.0090	0.0103	0.0117	0.0133	T/K	0.0090	0.0103	0.0117	0.0133
293.15	821.7				318.15	805.9	806.3	806.9	807.5
298.15	818.5	818.9			323.15	802.7	803.1	803.7	804.3
303.15	815.4	815.8	816.4		328.15	799.5	799.9	800.5	801.2
308.15	812.2	812.6	813.2	813.8	333.15	796.4	796.8	797.4	798.0
313.15	809.0	809.4	810.0	810.7	338.15	793.2	793.6	794.2	794.8

Thiourea (1) + 1-Hexanol (2)

	$\rho/(\text{kg m}^{-3})$					$\rho/(\text{kg m}^{-3})$			
	$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$		$x_1 =$	$x_1 =$	$x_1 =$	$x_1 =$
T/K	0.0079	0.0092	0.0106	0.0122	T/K	0.0079	0.0092	0.0106	0.0122
293.15	822.1				318.15	807.1	807.6	808.2	808.7
298.15	818.8	819.8			323.15	803.8	804.7	805.0	805.3
303.15	815.9	816.6	817.2		328.15	800.8	801.6	801.9	802.3
308.15	812.7	813.5	813.9	814.4	333.15	798.2	798.8	799.2	799.5
313.15	809.8	810.4	811.1	811.5	338.15	795.3	796.0	796.3	796.6

fraction, activity coefficient, enthalpy of fusion, solute heat capacity difference between the solid and liquid at the fusion temperature, triple point temperature of the solute, and equilibrium temperature, respectively, and $\Delta_{tr}H_1$ and $T_{tr,1}$ stand for the enthalpy of transition and transition temperature of the solute. In data reduction, the normal melting temperature and the enthalpy of fusion have been substituted into eq 2 for the corresponding values pertaining to the triple
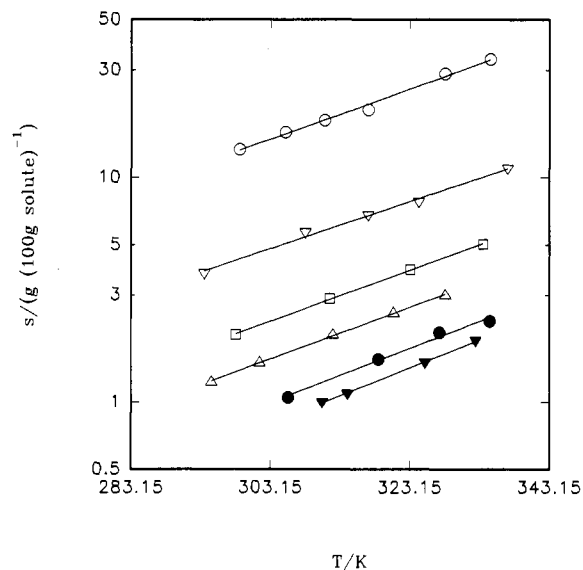

Figure 1. Solubility curves of thiourea in various alcohols: O, methanol; ∇, ethanol; □, 1-propanol; △, 1-butanol; ●, 1-pentanol; ▼, 1-hexanol.

Table 3. Experimental Solubilities s of Thiourea in Various Solvents

methanol		ethanol		1-propanol	
T/K	$s/(\text{g of solute}$ $(100\text{ g of}$ $\text{solvent})^{-1})$	T/K	$s/(\text{g of solute}$ $(100\text{ g of}$ $\text{solvent})^{-1})$	T/K	$s/(\text{g of solute}$ $(100\text{ g of}$ $\text{solvent})^{-1})$
298.66	13.40	293.66	3.75	298.17	2.00
305.23	16.00	308.13	5.70	311.66	2.90
310.88	18.10	317.17	6.80	323.25	3.90
317.19	20.10	324.45	7.80	333.65	5.05
328.18	29.00	337.16	11.00		
334.72	33.50				

1-butanol		1-pentanol		1-hexanol	
T/K	$s/(\text{g of solute}$ $(100\text{ g of}$ $\text{solvent})^{-1})$	T/K	$s/(\text{g of solute}$ $(100\text{ g of}$ $\text{solvent})^{-1})$	T/K	$s/(\text{g of solute}$ $(100\text{ g of}$ $\text{solvent})^{-1})$
294.66	1.23	305.65	1.05	310.55	1.00
301.59	1.50	318.66	1.55	314.18	1.09
312.11	2.00	327.43	2.05	325.33	1.50
320.80	2.50	334.64	2.30	332.62	1.88
328.25	3.00				

Table 4. Parameters for Eq 1 in Various Solvents

solvent	$10^3\alpha/$ $(\text{g of solute}$ $(100\text{ g of}$ $\text{solvent})^{-1})$	β/K^{-1}	solvent	$10^3\alpha/$ $(\text{g of solute}$ $(100\text{ g of}$ $\text{solvent})^{-1})$	β/K^{-1}
methanol	5.519	0.0260	1-butanol	0.559	0.0262
ethanol	3.420	0.0239	1-pentanol	0.334	0.0265
1-propanol	0.943	0.0257	1-hexanol	0.121	0.0290

point (5). The term involving the transition enthalpy and temperature is only needed when the solution temperature is below a solid-phase transition temperature. The third term of the right-hand side in eq 2 has little effect on the values of the activity coefficients and has therefore been neglected. The mole fractions of eq 3 were calculated with the following equation:

$$x_1 = \frac{sM_2}{100M_1 + sM_2} \tag{3}$$

where M_1 and M_2 are the molecular weight of the solute and

Table 5.   Activity Coefficients of Thiourea in Six Solvents

T/K	x_1	γ_1	x_1	γ_1
	Thiourea (1) + Methanol (2)		Thiourea (1) + Ethanol (2)	
293.15	0.0457	1.2781	0.0225	1.9859
298.15	0.0517	1.2407	0.0253	1.9555
303.15	0.0585	1.2012	0.0284	1.9226
308.15	0.0661	1.1559	0.0319	1.8874
313.15	0.0746	1.1171	0.0359	1.8500
318.15	0.0841	1.0730	0.0402	1.8107
323.15	0.0947	1.2079	0.0451	1.7695
328.15	0.1065	0.9820	0.0505	1.7268
333.15	0.1195	0.9356	0.0566	1.6826
338.15	0.1339	0.8889	0.0633	1.6371
	Thiourea (1) + 1-Propanol (2)		Thiourea (1) + 1-Butanol (2)	
293.15	0.0139	2.4683	0.0116	2.6511
298.15	0.0158	2.4728	0.0132	2.6081
303.15	0.0179	2.3849	0.0150	2.5626
308.15	0.0203	2.3394	0.0171	2.5146
313.15	0.0231	2.2918	0.0194	2.4643
318.15	0.0261	2.2419	0.0221	2.4119
323.15	0.0296	2.1902	0.0250	2.3575
328.15	0.0336	2.1368	0.0285	2.3012
333.15	0.0380	2.0818	0.0323	2.2434
338.15	0.0430	2.0252	0.0367	2.1840
	Thiourea (1) + 1-Pentanol (2)		Thiourea (1) + 1-Hexanol (2)	
293.15	0.0090	2.8999	0.0079	3.0299
298.15	0.0103	2.8551	0.0092	2.9726
303.15	0.0117	2.8077	0.0106	2.916
308.15	0.0133	2.7577	0.0122	2.8499
313.15	0.0152	2.7054	0.0141	2.7850
318.15	0.0173	2.6509	0.0162	2.7180
323.15	0.0198	2.5943	0.0187	2.6489
328.15	0.0225	2.5359	0.0215	2.5780
333.15	0.0256	2.4757	0.0249	2.5054
338.15	0.0291	2.4139	0.0286	2.4314

the molecular weight of the solvent, respectively. In this work the activity coefficient was calculated using eq 2 from the experimentally determined solution composition and temperature. Table 5 gives mole fractions, equilibrium temperatures, and activity coefficients. In nearly all the cases, positive deviations from ideal solution ($\gamma_1 > 1$) are observed. Also the deviation from ideal solubility increases with an increase in the number of carbon atoms in alcohols.

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