Original Article

Thermodynamic functions of dissolution of thiourea in triglycol

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Abstract : The solubility of thiourea in triglycol has been determined during a certain temperature range. The experimental data has been correlated with the modified Apelblat equation. The dissolution enthalpy and dissolution entropy have been calculated from the experimental data. The mutual interactions between solvent and solute have been discussed in brief. The data can be used for the preparation of thiourea, for example, methylthiouracil and thiamazole.
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INTRODUCTION

Thiourea is an important raw material,which is used in the synthesis of medicine, dyeware, dyeing auxiliaries, resin and compression moulding powder. Meanwhile, it also can work as vulcanization accelerator of rubber, flotation agents of metallic mineral, catalysts of the preparation of phthalic anhydride and fumaric acid, and rust inhibitor of mental. Owing to the extensive use of thiourea, it's significant to know its solubility in the solvents during its production and separation. In this article, we studied the solubility of thiourea in pure triglycol and the thermodynamic functions of the process, dissolution enthalpy and dissolution entropy, which may provide some essential data for the analysis of energy consumption.

EXPERIMENTAL

Materials

Thiourea, and triglycol were of analytical grade, and they were all obtained from Shanghai Chemical Reagent Co. and had the mass fraction purities of 0.995.

Solubility measurement

The solubilities of thiourea in pure triglycol were measured by a synthetic method at atmospheric pressure which can be seen in the previous article[1].

Test of apparatus

To prove the feasibility and the uncertainty of the measurement, the solubility of NaCl in water was measured and compared with the values reported in the literature[3]. The experimental data agreed with the reported values with a mean relative deviation of 0.18 % and 2.5 %, respectively.

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RESULT AND DISCUSSION

The measured solubilities of thiourea in pure triglycol solution at different temperatures can be seen in the TABLE 1. The temperature dependence of thiourea in pure triglycol is described by the modified Apelblat equation[4,5]

$$\ln x = A + \frac{B}{T/k} + C \times \ln(T/K) \tag{1}$$

Where x is the mole fraction solubility of thiourea, T is the absolute temperature, and A, B, C are the model parameters, which can be obtained from optimization and fitting.

TABLE 1 : Mole fraction solubilities of thiourea in triglycol

T/K	x	x_c	100RD	T/K	x	x_c	100RD
318.35	0.4561	0.4694	-2.92	339.35	0.4922	0.4922	0
321.65	0.4653	0.4715	-1.33	342.65	0.4957	0.4977	-0.4
324.55	0.4691	0.4737	-0.98	345.55	0.5	0.5031	-0.62
327.15	0.4749	0.4762	-0.27	348.95	0.5058	0.51	-0.83
331.05	0.4778	0.4805	-0.57	352.15	0.5109	0.5168	-1.15
333.55	0.4839	0.4836	0.06	354.85	0.5155	0.5231	-1.47
335.95	0.4845	0.4869	-0.5	357.75	0.5195	0.5302	-2.06

The values are listed in TABLE 2.

TABLE 2 : Parameters of thiourea in pure triglycol

A	B	C	R^2	10^3 RMSD	10^2 RAD
-85.07	3870.83	12.52	0.981	6.137	0.932

The relative deviation (RD), root-mean-square-deviation (RMSD), and relative average deviation (RAD) are defined in the previous articles. RD between the experimental values and the calculated values are listed in TABLE 1, and RMSD, RAD are listed in TABLE 2. Seen from TABLE 1, it can be found that the experimental data show good agreement with the calculated solubilities while the largest absolute value of RD is 2.92%, and the overall RMSD of the 14 data points which are correlated with the modified Apelblat equation for thiourea dissolving in pure triglycol. The RAD is only 0.932 %, and RMSD is just 6.137‰, which indicate that the Apelblat equation is fit to correlate the solubility data of thiourea in pure triglycol.

Thermodynamic functions related with solubility are mainly dissolution enthalpy and dissolution entropy, namely ΔH and ΔS, which can be obtained through a series of equations. According to a pseudochemical reaction process, the fundamental thermodynamic relation and the derivation[6-14], the molar enthalpies of dissolution ΔsolH and the molar entropy of dissolution Δ_{sol}S can be obtained:

$$\Delta_{sol}H = R \times T \times (C - \frac{B}{T}) \tag{2}$$

$$\Delta_{sol}S = R \times (C - \frac{B}{T}) \tag{3}$$

According to the parameters of modified Apelblat equation listed in TABLE 2, Δ_{sol}H and Δ_{sol}S can be calculated by Equation (3) and Equation (4), which are listed in TABLE 3

TABLE 3 : Δ_{sol}H(kJ mol⁻¹) and Δ_{sol}S(J mol⁻¹ K⁻¹) for thiourea in triglycol

T/K	$\Delta_{sol}H$ (kJ mol⁻¹)	$\Delta_{sol}S$ (J mol⁻¹ K⁻¹)	T/K	$\Delta_{sol}H$ (kJ mol⁻¹)	$\Delta_{sol}S$ (J mol⁻¹ K⁻¹)
318.35	0.96	3.00	339.35	3.14	9.25
321.65	1.29	4.03	342.65	3.48	10.17
324.55	1.60	4.93	345.55	3.78	10.96
327.15	1.87	5.72	348.95	4.14	11.86
331.05	2.28	6.87	352.15	4.47	12.70
333.55	2.53	7.60	354.85	4.75	13.39
335.95	2.78	8.29	357.75	5.05	14.13

It can be seen from TABLE 3 that both Δ_{sol}H and Δ_{sol}S increase when the temperature increases. Also, from TABLE 3, we can see that the process of thiourea dissolving in pure triglycol at the temperature range is endothermic, Δ_{sol}H>0.

Thiourea needs to absorb energy to overcome the interactions between the solutes molecular when thiourea dissolves in pure triglycol, thus thiourea molecular can diffuse into solvent. It is a physical process, and has an endothermic effect. Meanwhile, owing to the oxhydryl existing in triglycol molecular and amidogen in thiourea molecular, the dissolution process of such a solute in solvents involves some forces such as solvent polarization, hydrogen bond, electrostatic, and stereoscopic effect, etc, which make the process exothermic. On the whole, the process is endothermic, and the reason might attribute to the fact that the interactions of the solute thiourea molecular are more powerful than the interactions between the thiourea molecular and the triglycol; so in order to overcome the interactions between the solute molecular, the system needs to absorb

heat from the surroundings. Therefore, the process is an endothermic effect. As for the dissolution entropy $\Delta_{sol}S$, entropy is defined as the degree of chaos of the system. Before adding solute thiourea into the solvent triglycol, the system is in order, and has a very low degree of chaos. However, after putting the solute into the solvent, the solute molecular disrupts the alignment of the solvents molecular and therefore the degree of the system reduced while thiourea dissolves in pure triglycol.

CONCLUSION

The solubilities of thiourea in pure triglycol were measured, and the experimental data were correlated with the Apelblat equation, and the dissolution enthalpy $\Delta_{sol}H$ and dissolution entropy $\Delta_{sol}S$ were estimated. The RAD is 0.932%, and RMSD is 6.137 ‰, which indicate the calculated data show good agreement with the experimental data. The positive $\Delta_{sol}H$ and $\Delta_{sol}S$ reveal the process is endothermic and entropy-driven. The experimental solubility and correlation equation in this work can be used as essential and basic data for the preparation of thiourea, for example, methylthiouracil and thiamazole.

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