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A Calorimeter for Measuring the Enthalpy of Solution of Solid Solutes in Supercritical Fluids and Study on CO_2-Naphthlene System

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Abstract: An apparatus for measuring the enthalpy of solution of solids in supercritical fluids (SCFs) was constructed. The enthalpy of solution (ΔH) of naphthalene in supercritical (SC) CO_2 was measured at 308.15 K in the pressure range from 8~11 MPa. It was found that ΔH was negative in the pressure range from 8 to 10 MPa, and the absolute value of ΔH decreases with increasing pressure. However, ΔH became positive at the pressures higher than 10 MPa. This unusual phenomenon can be explained by clustering between CO_2 and naphthalene.

Keywords: Solution enthalpy, supercritical fluid, molecular interaction

Supercritical fluids (SCFs) have some unique properties[1] It has been known that SCFs have very strong ability to dissolve low volatile compounds, which is the basis of SCF technology. However, the mechanism of SCFs to dissolve solutes is not very clear. Enthalpy of solution of solutes in SCFs can provide useful information for studying the mechanism. In this work, we built a calorimeter and ΔH for the dissolution of naphthalene in supercritical CO_2 was determined. This kind of work was not found in a literature survey.

CO_2 with a purity of 99.995% was supplied by Beijing Analytical Instrument Factory. Naphthalene was A.R. grade produced by Beijing Chemical Plant. The apparatus built in this work can determine simultaneously the solubility of solid solutes in SCFs and the enthalpy of solution. It is based on the principle that the temperature of a vessel with a solute will change when a SCF flows through the vessel and dissolves some of the solute. The ΔH can be easily calculated on the basis of the temperature change(after calibrating the heat exchange), the heat capacity of the vessel, and the mass of the solute dissolved. The apparatus consisted mainly of a calorimeter vessel, a thermostat, an electric calibrator, a precision thermistor thermometer, a pressure-controlled SCF cylinder, and a sample collector which was used to collect the dissolved solute. We will not give more detailed description for the apparatus in this short paper.

This apparatus was used to determine the heat of dissolving known mass of solutes at equilibrium condition. Thus, the keys for reliability of the data are heat calibration and solubility determination. Electric method is reliable for heat calibration, and the calibrator was tested by determining the heat capacity of water using the calorimeter. To verify the reliability of solubility data we compared our results with those reported by other authors [2,3], and the agreement was good, as shown in **Figure 1**. **Figure 2** shows the dependence of ΔH on pressure. The uncertainty of the data is about ±1.0 kcal/mol. It can be seen that ΔH is negative in the pressure range from 8.0 to 10.0 MPa, *i.e.*, the solution process is exothermic. The absolute value of ΔH decreases dramatically as the pressure changes from 8.0 MPa to 8.5 MPa. ΔH becomes positive when pressure exceeds 10 MPa. In order to explain this phenomenon, we divide ΔH into two parts, *i.e.*, $\Delta H = \Delta H_1 + \Delta H_2$. ΔH_1 is enthalpy of sublimation of naphthalene, which is positive. ΔH_2 is the enthalpy of solution of gaseous naphthalene in SC CO_2, which should be negative because interaction between CO_2 and naphthalene is very strong, even clusters are formed[1]. At the lower pressures, the clustering is more significant and thus ΔH_2 is dominant and ΔH is negative. At 308.15 K, the extent of clustering decreases sharply with pressure[4], which results in dramatic decrease of the absolute value of ΔH.

Figure 1 Solubility of naphthalene in SC CO_2 at 308.15 K

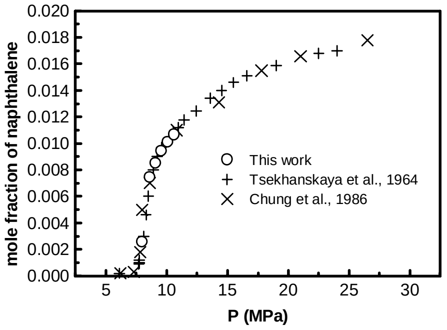
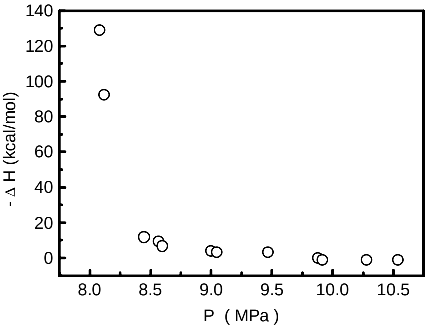


Figure 2 Dependence of ΔH on pressure at 308.15 K



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