Heat of Solution from Solubility Measurements

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Abstract:

When a solute is dissolved in a solvent to form a solution, heat is either absorbed or evolved. The heat change per mole of solute is called heat of solution. The heat of solution of naphthalene-toluene binary mixture is determined by its both molal and/or molar saturation solubility at different temperatures. Even though solubility studies are reported, the molal heat of solution from solubility measurements is not known and we are reporting it for naphthalene-toluene binary mixture solution. Here, the method is described and in comparison to molar heat of solution.

Keywords: Heat of solution, solution enthalpy, saturation solubility

Introduction

During a chemical reaction, energy can be transferred as heat and thermochemistry involves measurement of such energy being transferred. The heat changes accompanying a transformation depend on path chosen, but if the process is carried out at constant pressure or constant volume, the heat changes involved have definite values. It is for this reason that the processes are conducted at constant pressure or at constant volume conditions. The Van’t Hoff equation[1,2] relates the equilibrium constant variation with temperature as a function of the enthalpy of the system, assuming the enthalpy change is independent of temperature.

$$\frac{d\ln k_p}{dT} = \frac{\Delta H^o}{RT^2}$$

$$\int_{1}^{2} d\, lnk_p = \frac{\Delta H^0}{R} \int_{T_1}^{T_2} \frac{1}{T^2}\, dT$$

$$ln\frac{k_{p2}}{k_{p1}} = -\frac{\Delta H^o}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

where, K_p is the equilibrium constant in terms of pressure and ΔH^o is the enthalpy change of the reaction when the reactants and products are in their standard states. Thus, if we know equilibrium constant at two different temperatures, enthalpy of solution can be determined. In general, the enthalpy change does not vary appreciably with pressure and ΔH^o can be replaced by ΔH, the enthalpy change of reaction at moderate pressures. So, we can write van't Hoff equation as,

$$\frac{dln\, k_p}{dT} = \frac{\Delta H}{RT^2}$$

The influence of temperature on solubility can be expressed by van't Hoff equation,

$$\frac{dln\, m_s}{dT} = \frac{\Delta H}{RT^2}$$

where m_s is solubility of the salt in moles per 1000 gm of solvent and ΔH is the molal heat of solution. On integration gives,

$$\ln m_s = \frac{-\Delta H}{R}\frac{1}{T} + Constant$$

A plot of ln m_s versus $\frac{1}{T}$ gave a straight line with slope = $\frac{-\Delta H}{R}$.

In the experiment, heat of solution of naphthalene in toluene is determined by measuring saturation solubility at different temperatures. Here solubility can also be expressed[3] by mole fraction of naphthalene in toluene at different temperatures. The solubility behavior of compounds depends on relative strength of their intermolecular interactions. Even though naphthalene and toluene are non-polar aromatic compounds, the forces of interactions between them are weak vander Waals forces. When these two solvents are mixed, the intermolecular forces between naphthalene-naphthalene, toluene-toluene and toluene-naphthalene are not identical strength. Hence enthalpy of mixing is not zero.

The solubility of a solid in an ideal solution depends on temperature, melting point of solid and molar heat of fusion. In an ideal solution, heat of solution is equal to heat of fusion, which is assumed to be constant and independent of temperature. Ideal solubility is not affected by nature of solvent. For an ideal solution of a solid in a liquid, the mole fraction solubility is given by,

$$ln\ X = \frac{-\Delta H_f}{R}\left(\frac{T_0 - T}{T\ T_0}\right)$$

Where X is ideal solubility of solute expressed in mole fraction, T_0 is the melting point of solid solute and T is the absolute temperature of solution. In an ideal solution, liquid solute is miscible in all proportions with the solvent and so the equation is not valid when $T > T_0$. The above equation can also be written as,

$$ln\ X = \frac{-\Delta H_f}{R}\frac{1}{T} + Constant$$

Or, $$ln\ m_s = \frac{-\Delta H_f}{R}\ \frac{1}{T} + Constant$$

A plot of ln m_s or ln X versus $\frac{1}{T}$ will be a straight line with slope equal to $\frac{-\Delta H_f}{R}$. Since the chemical potential in real cases depends on activity rather than on molality, the results are expected to differ from ideal case.

Materials and Methods

All chemicals used were analytical grade. The solute naphthalene was added to a boiling tube which contains a stirrer (Steel) and a thermometer which can measure temperature to an accuracy of 0.1 ^{0}C and are inserted through a cork into the boiling tube. The solvent toluene is added to the boiling tube through a burette. It is important that both solid and solution phases should be in dynamic equilibrium at all temperatures. So experiment is beginning with tempering the saturated solution.

To the boiling tube, weighed 7gm (0.0546 mol) of naphthalene and added 2 ml of toluene. The thermometer is introduced so that the bulb is immersed in the liquid. The solution is stirred and noted the solubility of naphthalene. Since it is not completely soluble, the mixture is gently warmed in hot water and transferred into an air jacket. The solution is stirred until naphthalene crystals completely dissolved and the temperature is noted at which the last crystals go into solution. Then, the solution is allowed to cool until crystals reappear and again the temperature is noted. The average of the two temperatures is calculated and thus, recorded the saturation solubility temperature. The mixture is re-heated just enough to cause the crystals to re-dissolve again to narrow the discrepancy between the temperature readings. In cases were crystals not appeared at room temperature, cold water bath is used to cool the solution until crystals appear, followed by allowing the solution to warm up until the crystals re-dissolve. Here also, it is repeated again to narrow the discrepancy between the temperatures at which the crystals disappear and reappear.

The experiments are repeated with other volumes of toluene and in each case average saturation solubility temperature is noted. Mole fraction (X) and molal solubility (m_s) of naphthalene is calculated in each case. A graph is plotted between ln X or ln m_s against $\frac{1}{T}$ (K$^-$

^{1}) and from the slope of the graph, the heat of fusion of naphthalene is calculated. The data is fitted by the linear regression analysis using least squares method in Microsoft Excel and the coefficient of the least square method is computed.

Results and Discussion

A solution is a homogeneous mixture of two or more components. The component which is usually present in largest proportion is called the solvent and the second component, which is dissolved in the solvent is called solute. The solutions can be different kinds:: gases in gases (example: air), liquid in liquids (example: gasoline), gases in liquids (example: soda drinks), solids in solids (example: alloys), and solids in liquids (example: salt water)[1]. This experiment will involve a solution formed with a solid solute and a liquid solvent.

Solubility of a solid in a liquid depends on temperature. At a given temperature, if maximum amount of solute is dissolved in a given amount of solvent, then it is called saturated solution. This maximum amount of dissolved solute can be expressed quantitatively in units of molality and molarity[3]. The factors that can affect solubility of a solute in a solvent are, (1) the nature of solute and solvent and (2) temperature. Polar and ionic solutes are soluble in polar solvents and non polar solutes are soluble in non-polar solvents. The temperature of the solvent generally has a marked effect on the amount of solute that can dissolve.

The solubility behaviour of the compounds and the heat of solution depend greatly on the relative strength of their intermolecular interactions. Both naphthalene and toluene are non polar compounds and the attraction that exists in naphthalene and toluene are van der waals forces. When they are mixed, enthalpy of mixing is not zero because the strength of forces between solute-solute, solute-solvent and solvent-solvent are not identical. In such a case, the solution cannot be considered as ideal.

In the experiment, different volume of toluene is added to 0.0546 mol of naphthalene and saturation solubility temperature (T) is determined (Table 1). It is also obtained for additional volumes of toluene. The mass of toluene is calculated from its volume and density. Molal solubility (m_s) is calculated at different temperatures and a graph is plotted with $\ln(m_s)$ versus $\frac{1}{T}$ in K^{-1} (Figure 1). The molal heat of fusion of naphthalene obtained is 49.89 kJ/kg of solvent.

Table 1. Molal saturation solubility of naphthalene in toluene at different temperatures

Moles of Naphthalene	Volume of toluene (ml)	Saturation solubility temperature (K)	$\frac{1}{T}$ (K^{-1})	Mass of toluene (kg)	Molal solubility (m_s) (mole/kg solvent)	$\ln(m_s)$
0.0546	2	339.75	0.00294	0.00174	31.38	3.446
0.0546	2.5	336.75	0.00297	0.0022	24.82	3.212
0.0546	3	333.75	0.0030	0.00261	20.92	3.041
0.0546	3.5	330.75	0.00303	0.00305	17.90	2.885
0.0546	4	328.4	0.00305	0.00348	15.69	2.753
0.0546	4.5	325.75	0.00307	0.00392	13.93	2.634
0.0546	5	323.25	0.00309	0.00435	12.55	2.530

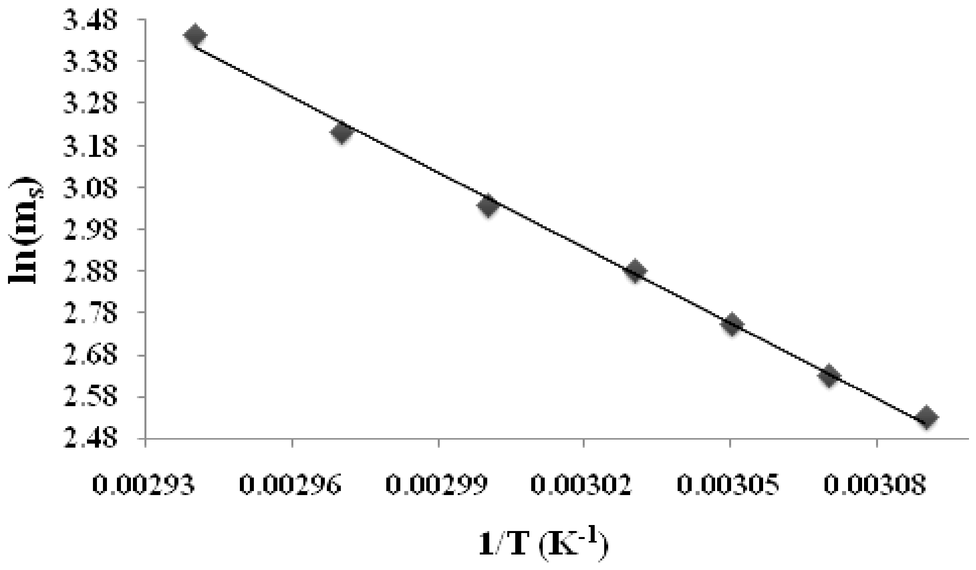

Figure 1. Plot of ln(m_s) against $\frac{1}{T}$ (K^{-1}) of naphthalene in toluene.

Mole fraction solubility of naphthalene is also calculated at different temperatures (Table 2) and a graph is plotted with ln(X) versus $\frac{1}{T}$ in K^{-1} (Figure 2). The molar heat of fusion of naphthalene obtained is 17.8 kJ/mol, which is very close to the reported value of 18.8 kJ/mol[4,5].

Table 2. Mole fraction solubility of naphthalene in toluene at different temperatures

Moles of Naphthalene	Moles of toluene	Saturation solubility temperature (K)	$\frac{1}{T}$ (K^{-1})	Mole fraction of naphthalene (X)	ln(X)
0.0546	0.0189	339.75	0.00294	0.74	-0.3011
0.0546	0.0236	336.75	0.00297	0.70	-0.3567
0.0546	0.0283	333.75	0.0030	0.66	-0.4155
0.0546	0.0330	330.75	0.00303	0.62	-0.4780

0.0546	0.0378	328.4	0.00305	0.59	-0.5276
0.0546	0.0425	325.75	0.00307	0.56	-0.5798
0.0546	0.0472	323.25	0.00309	0.54	-0.6162

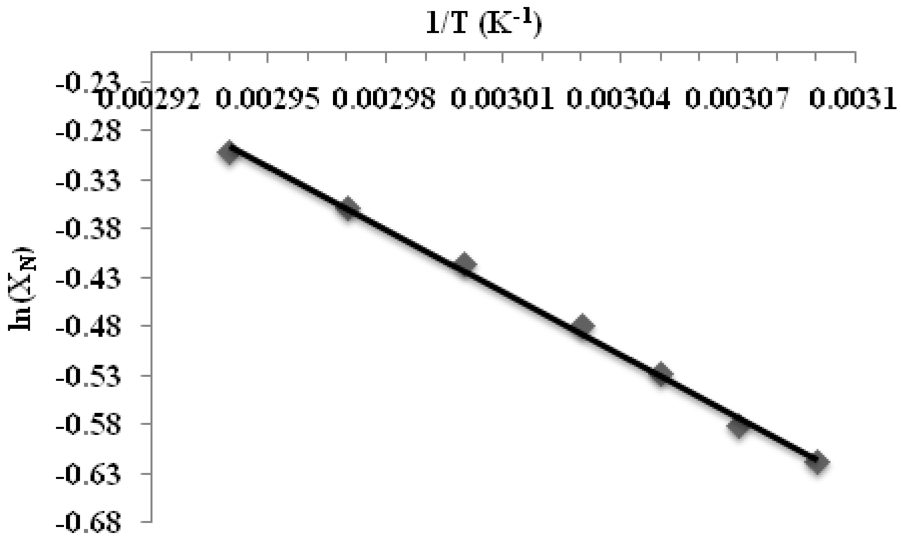

Figure 2. Plot of ln(X_N) against $\frac{1}{T}$ (K^{-1}) of naphthalene in toluene.

From the experiment both molal and molar heat of fusion can be calculated. The heat of fusion is not zero, which implies that the solubility of naphthalene in toluene is not exactly ideal. Solubility data is widely used in chemistry and related fields of science and engineering for many different purposes. For some intended purposes, highly precise data are required; but for others, order-of-magnitude estimate is satisfactory[3].

Conclusion

The solubility behavior of naphthalene in toluene is not ideal. The study of solubility behavior of different kinds of compounds in different solvent system is important that it gave information about enthalpy content. Such studies can provide that the system will be a better source for making an *in situ* heating pad.

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