Solubility of Dimethylamine in o-Dichlorobenzene under Isoproturon Synthesis Conditions†

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Solubilities of anhydrous dimethylamine (DMA) were measured in o-dichlorobenzene (o-DCB) at temperatures of 293–413 K under a total pressure of 95 kPa. The temperature dependence of the gas solubility was used to determine the partial molal Gibbs energy, partial molal enthalpy, and partial molal entropy of solution. The results have been useful in the analysis of the reaction kinetics of the reaction of cumylurea with dimethylamine. Modeling of isoproturon synthesis in a bubble column reactor at atmospheric pressure has been carried out using the solubility data obtained.

Introduction

Isoproturon, an important herbicide in wheat crops, is prepared by the transamidation of cumylurea with anhydrous dimethylamine (DMA). The efficiency of the process depends on the temperature of the reaction and the solubility of DMA at that temperature in o-dichlorobenzene (o-DCB), a solvent chosen for use in the process. A search of the literature revealed that there was no report on the solubility of DMA in o-DCB. The IUPAC compilation (1985) does not contain any data on this system (*1*). Without knowledge of such solubility data, it is not possible to interpret the kinetics of heterogeneous reactions of transamidation nor to model the rate of conversion. Hence, the solubilities of DMA in o-DCB over the temperature range 293–413 K were measured. The results have been used in the process development work on isoproturon herbicide (*8*).

Experimental Section

Anhydrous dimethylamine of 99.9% purity supplied by M/s Rashtriya Chemicals & Fertilizers, Bombay, and o-dichlorobenzene of 99.5% purity supplied by M/s Sisco Research Laboratory, Bombay, were used. The impurities in o-DCB are meta and para isomers, together constituting 0.5% as determined by GC on a Hewlett-Packard Model 5880A with an SE-30 column with an oven temperature of 373 (initial) to 433 K (final) with nitrogen as the carrier gas.

The solubility results of this work have been given in Table I. The solubilities were measured with an apparatus similar to that used by Haimour (*2*). It consists of an equilibrium cell (absorption flask) of 250 cm^3 capacity with a magnetic stirrer, housed in a thermostated oil bath. The temperature of the whole unit was kept constant within ±0.2 K by means of a thermistor thermometer and circulation of oil. o-DCB (100 cm^3) was placed in the equilibrium cell, and the system was flushed with anhydrous DMA to remove air from inside the system. Then DMA was directly bubbled at a constant rate through the liquid in the equilibrium cell for 4–5 h, maintaining a constant temperature and pressure (95 ± 0.5 kPa). After the DMA bubbling was stopped, the mercury levels were observed for more than 1 h or until there were no changes. Then it was assumed the system had attained equilibrium. Samples (5–10 g) were drawn out of the equilibrium cell, and the dissolved DMA was converted into its hydrochloride by running the samples immediately into an excess of hydrochloric acid solution. The analysis of DMA was made by determining the excess acid by titration with standard alkali as per the method reported (*3*). Care was taken during sampling to avoid any loss of gas. This sampling and analysis were carried out a number of times. The values obtained were consistent. The solubility results are given in Table I. The reliability of the experimental method was checked by measuring the solubility of DMA in chlorobenzene for which reported values (*4*) are available.

Table I. Solubility of Dimethylamine (2) in o-Dichlorobenzene (1)

	x_2			x_2	
T/K	exptl	calcd	T/K	exptl	calcd
293	0.5961	0.5956	373	0.037	0.0374
313	0.2679	0.2722	393	0.0231	0.0212
333	0.1380	0.1331	413	0.013 71	0.0125
353	0.067	0.0688			

The solubility of DMA in chlorobenzene at 293 K is 0.51 compared with the reported value of 0.52 at 293 K and 93 kPa. The estimated maximum experimental error in the determinations is approximately ±2% of the reported mole fraction. The solubility was expressed as the mole fraction of dimethylamine in solution ($\ln x_2$) for a total pressure 95 kPa.

Results and Discussion

The solubility of dimethylamine ($\ln x_2$) in o-dichlorobenzene is given in Table I. The range of temperatures studied was between 293 and 413 K. The results were fitted (*5*) to the equation

$$\ln x_2 = a + b/(T/\mathrm{K}) + c \ln (T/\mathrm{K}) \quad (1)$$

The values of constants a, b, and c obtained were 34.635, 1451.96, and −7.0612, respectively. The calculated values (Table I) are in close agreement with the experimental values. Our previous method of correlation (*6*) is not applicable to this system, since the volume fraction of solute is not negligible and in some of the cases it is found to be more than 0.1.

The partial molal Gibbs energy $\Delta G°$, partial molal enthalpy $\Delta H°$, and partial molal entropy $\Delta S°$ were calculated (*7*) by means of the equations given below:

$$\Delta G° = -RT(a + b/T + c \ln T) \quad (2)$$

$$\Delta H° = RT(-b + cT) \quad (3)$$

$$\Delta S° = R(a + c \ln T + c) \quad (4)$$

The values obtained were $\Delta G° = 1.784$ kJ mol^{-1}, $\Delta H° = -29.523$ kJ mol^{-1}, and $\Delta S° = -0.105$ kJ mol^{-1} K^{-1}.

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The solubility decreases with an increase in temperature. The results have been useful in the design of a bubble column reactor at atmospheric pressures in the synthesis of isoproturon (*8*).

Registry Numbers Supplied by Author. Dimethylamine, 124-40-3; *o*-dichlorobenzene, 95-50-1.

Literature Cited

(1) *Solubility Data Series*; Pergamon Press: New York, 1985; Vol. 21.
(2) Haimour, N. *J. Chem. Eng. Data* **1990**, *35*, 177.
(3) Lowen, W. K.; Baker, H. M. *Anal. Chem.* **1952**, *24*, 1475.
(4) *Solubility Data Series*; Pergamon Press: New York, 1985; Vol. 21, p 175.
(5) Lopez, M. C.; Gallardo, M. A.; Vrieta, J. S.; Losa, C. G. *J. Chem. Eng. Data* **1987**, *32*, 472.
(6) Radhakrishnan, K.; Ramachandran, P. A.; Brahme, P. H.; Chaudhari, R. V. *J. Chem. Eng. Data* **1983**, *26*, 1.
(7) Dack, R. J. *Techniques of Chemistry and Physics (Solutions and solubilities)*; Weissberger: New York, 1975.
(8) Mohan, K.; Venkataratnam, R. V.; Rajan, G. T.; Bhalerao, U. T.; Koteswara Rao, S.; Rao, M. P.; Narsaiah, B.; Bal Reddy, B.; Eshwar Rao, M. Indian Patent No. 162896, Feb 27, 1985.

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