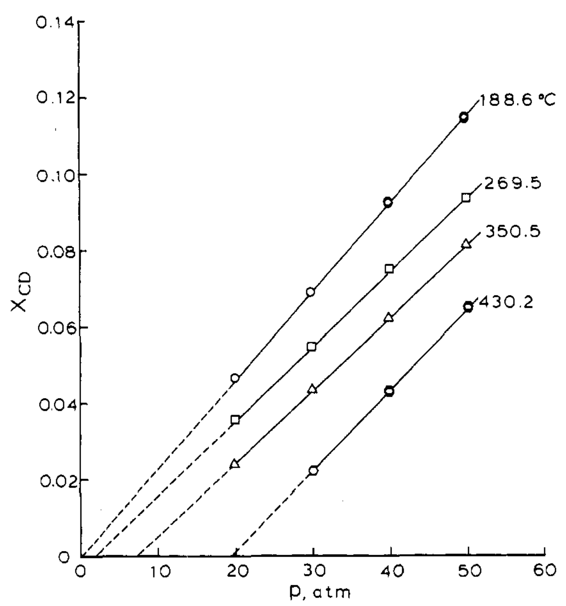

Figure 4. Solubility of CO_2 in quinoline.

Results

Table I presents compositions of the coexistent vapor and liquid phases in CO_2 plus *m*-cresol mixtures at the temperatures 189.5, 269.3, 351.3, and 391.5 °C. The pressures are from 20 to 50 atm for each of the three lower temperatures. However, at the highest temperature, only two pressures at 40 and 50 atm were measured because of the high vapor pressure of *m*-cresol.

Figures 1 and 2 show the saturated compositions of the vapor and the liquid phases, respectively, for mixtures of CO_2 plus *m*-cresol as a function of the total pressure. Individual samples are plotted in the figures as separate points where they can be differentiated. The end points at $X_{CD} = 0$ in Figure 2 correspond to the vapor pressures of *m*-cresol, which are available from Simnick and co-workers (*3*).

Table II presents the results for the CO_2 plus quinoline system at the temperatures 188.6, 269.5, 350.5, and 430.2 °C and pressures up to 50 atm. The equilibrium compositions are shown in Figure 3 for the vapor phase and Figure 4 for the liquid. The vapor pressure data indicated in Figure 4 were taken from Sebastian et al. (*1*).

The reported phase compositions are the averages of at least two observations at a fixed T and p. The deviations of the direct observations from the average are generally within 0.5% in mole fraction of CO_2. The average values of x and y are used to calculate the K values.

Acknowledgment

Mark J. Horvath assisted in measuring the solubilities of CO_2 in *m*-cresol and in quinoline at ambient conditions.

Glossary

K	vaporization equilibrium ratio
p	pressure, atm
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Subscripts

CD	carbon dioxide
Cr	*m*-cresol
Q	quinoline

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Solubility of Benzoic Acid in Aqueous Polyethylene Glycol Solutions

Haribansh Sahay, Surendra Kumar, Siddh N. Upadhyay,* and Yogendra D. Upadhya

Department of Chemical Engineering and Technology, Institute of Technology,
Banaras Hindu University, Varanasi-221005, India

Solubility of benzoic acid in aqueous solutions of polyethylene glycols (PEG) (mol wt = 4000, 6000, and 20 000) containing 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0% polymers by weight are reported in the temperature range 30–55 °C. The solubility in the polymer solutions at a given temperature is higher than that in water, increases with increasing polymer concentration and decreasing polymer molecular weight, and seems to approach a constant value at higher polymer concentrations.

Introduction

Increasing occurrence of non-Newtonian fluids in many process industries and our other day-to-day activities as well as in biological systems has generated interest in the study of transport characteristics of these complex fluids. Fundamental mass-transfer studies with such fluids are often made by using a sparingly soluble solid solute such as benzoic acid. Analysis of raw experimental data in all such cases needs accurate values of system properties.

This communication reports the solubility of benzoic acid in aqueous solutions of polyethylene glycols (PEG). These results will also be useful to the pharmaceutical industry. The results reported here have been obtained adjunct with the mass-transfer investigations conducted with aqueous polyethylene glycol solutions and benzoic acid.

Experimental Section

Conductivity-grade distilled water used for making solutions was prepared in the laboratory. Polyethylene glycols (PEG) used

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* Present address: Department of Energy Engineering, College of Engineering, UICC, Chicago, IL 60680.

Table I. Solubility of Benzoic Acid in Aqueous Polyethylene Glycol Solutions

concn, wt %	temp, °C 30	35	40	45	50	55
			Mol Wt = 4000			
0.5	4.402	5.210	6.021	7.105	8.403	9.509
1.0	4.800	5.410	6.404	7.712	8.907	10.201
2.0	5.407	6.031	7.152	8.431	9.812	11.101
3.0	5.901	6.701	7.600	8.903	10.706	11.903
4.0	6.100	7.100	7.951	9.407	11.503	12.91
5.0	6.411	7.451	8.602	10.307	12.102	13.503
6.0	6.603	7.607	8.901	10.211	12.207	13.81
			Mol Wt = 6000			
0.5	4.200	4.903	5.800	6.807	7.910	8.901
1.0	4.510	5.200	6.010	7.200	8.230	9.607
2.0	5.107	5.803	6.610	7.800	8.906	10.21
3.0	5.400	6.210	7.110	8.220	9.603	11.11
4.0	5.810	6.750	7.600	8.810	10.22	11.50
5.0	6.002	7.210	8.010	9.207	10.91	12.20
6.0	6.200	7.250	8.303	9.520	11.10	12.52
			Mol Wt = 20 000			
0.5	4.110	4.750	5.610	6.590	7.420	8.750
1.0	4.400	5.120	5.980	6.920	8.100	9.410
2.0	4.910	5.421	6.412	7.302	8.410	9.911
3.0	5.200	6.011	6.803	7.411	9.023	10.5
4.0	5.601	6.307	7.210	7.904	9.409	10.81
5.0	5.903	6.400	7.617	8.521	9.913	11.203
6.0	6.090	6.612	8.021	8.620	10.101	11.513

were PEG (mol wt = 4000, Lab.-Chem. Industries, Bombay, India) and PEG (mol wt = 6000 and 20 000, BDH Chemicals, Poole, UK). The benzoic acid (AR) used was obtained from IDPL, Hyderabad, India. Aqueous polymer solutions were prepared in batches of 6 L by dissolving a known amount of polymer in an appropriate amount of distilled water and were allowed to stand for 36 h before use in the actual experiments.

Solubilities of benzoic acid in each of these solutions at different temperatures were determined by "equilibrated solution" technique as described elsewhere (*1*). Measurements were made with polymer solutions containing 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0% polymers by weight in the temperature range 30–55 °C. The thermostated bath used was capable of providing a temperature control with an accuracy of ±0.1 °C. Special care was taken to exclude carbon dioxide from all of the systems during experimentation. All measurements were made in quadruplicate and the reproducibility was within ±1–2% of the mean value.

Results and Discussion

The measured solubilities of benzoic acid in the aqueous solutions of the three polymers investigated are listed in Table I. The solubility in aqueous polymer solutions is more than that in water and increases to a constant value with increasing polymer concentration and decreases with increasing polymer molecular weight.

The observed enhancement in the solubility in the polymer solutions over that in water and its approach toward a constant value at higher polymer concentrations at any particular temperature are due to the reasons mentioned elsewhere (*2*). The decrease in the solubility with increasing polymer molecular weight is once again due to decrease in the solvolysis of the solute molecules with increasing polymer molecular weight. Thermodynamically speaking, increasing polymer molecular weight results in a decrease in entropy of mixing and in turn increases the free energy of mixing and hence a decrease in the solubility values.

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Several Properties of 1,1,3,3-Tetramethylurea–Water Systems

Chigosim Okpala, Anthony Guiseppi-Elie, and Dow M. Maharajh*

Department of Chemistry, The University of the West Indies, St. Augustine, Trinidad, West Indies

Dielectric constants, viscosities, densities and partial molar volumes for aqueous tetramethylurea mixtures have been determined at 25 °C. Where possible, the data are compared with previously reported values. Molar polarization for the tetramethylurea–water mixtures are shown to be linear functions of the mole percent through the complete range of the solvent mixtures.

The data presented here were accumulated during the course of an extensive investigation of conductances in the tetramethylurea–water systems. Despite the usefulness of the material as a good solvent for many organic substances, physicochemical studies on tetramethylurea solutions are very few. Tetramethylurea is one of the few urea derivatives which are liquid at room temperatures and acts only as a hydrogen-bond acceptor without an ability as a proton donor. The solute–solvent interactions in tetremethylurea solutions will be discussed.

Experimental Section

The dielectric constants were measured at 1 MHz by a dekameter (Dk 300, Karl Kolb) with a digital readout.

Tetramethylurea (Sigma Chemical Co.) was used after being refluxed with calcium hydride under nitrogen atmosphere and distilled at 10 mmHg. Densities of aqueous solutions were measured with an Ostwald-type pycnometer at 25 °C, and partial molar volumes were calculated. Viscosity coefficients for the solutions were measured with an Ostwald-type viscometer at 25 °C.

Temperature regulation at 25 ± 0.001 °C for the above measurements was obtained in a thermostatically controlled water bath with the absolute temperature determined by a

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