T temperature, K

ϕ isothermal throttling coefficient, J mol^{-1} bar^{-1}

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Solubility of Hydrogen in α-Methylstyrene

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Prior studies of the solubility of hydrogen in α-methylstyrene at atmospheric pressure give results that differ by 30 to 40%. In an attempt to resolve this deviation, solubilities were measured from 15 to 74 °C. The results, which were reproducible within 3%, fall about midway between the earlier data.

The liquid-phase, catalytic hydrogenation of α-methylstyrene to cumene is often used as a model reaction for reactor studies, for example, in fixed (*1*, *2*, *4*) and in trickle beds (*5*). An accurate value of the hydrogen concentration in the liquid styrene is necessary for quantitative interpretation of such reactor investigations. However, reported solubilities (*3*, *5*) differ by 30–40% possibly because such low concentrations are difficult to measure accurately. In an attempt to resolve this uncertainty, we have carefully measured the solubility at atmospheric pressure of hydrogen over the temperature range 15–74 °C.

Experimental Section

The saturated solutions were prepared from α-methylstyrene (Dow Chemical Co.) with a stated purity of 99.2% and hydrogen (Liquid Carbonic Corp.) with a stated purity of 99.99%. The liquid was saturated at atmorpheric pressure by bubbling pure H_2 for at least 10 h through 800 cm^3 of styrene contained in a 1000-cm^3 Pyrex flask. The flask was immersed in a water bath whose temperature could be controlled to ±0.1 °C. To test the assumption of saturation, measurements were made first at successively higher temperatures and then at successively lower temperatures, with 10 h allowed for saturation at each temperature. Since the solubility was found to increase continuously with temperature, this procedure provided a means of approaching saturation first by absorption and then by desorption. The hydrogen concentration was determined by analyzing liquid samples in gas chromatographs using a 6 m long, 0.63 cm o.d. column packed with 20–40 mesh, 5A molecular sieve particles. Nitrogen was used as the carrier gas. The purity of the nitrogen (liquid Carbonation Corp.) was given as 99.996%.

Table I. Gas Chromatograph Operating Conditions

GC Model	1420
Column temp, °C	100
Injector temp, °C	170
Detector temp, °C	160
Detector current, mA	100
Carrier gas flow rate,[a] cm^3/min	25
Attenuator setting	2

[a] At 25 °C, 1 atm.

Table II. Experimental Results, Individual Solubility Measurements

Hydrogen Solubility, (g-mol/cm^3) × 10^6						
14.8 °C	33.8 °C	41.0 °C	48.5 °C	58.5 °C	65.5 °C	73.5 °C
2.39	2.74	2.79	3.08	3.09	3.18	3.29
2.43	2.74	2.86	3.10	3.12	3.17	3.26
2.45	2.78	2.82	3.06	3.09	3.16	3.24
2.43	2.78	2.83	3.06	3.16	3.16	3.27
	2.70	2.88	3.08	3.11	3.16	
			3.04	3.09		

A special, gastight, 50-μL Hamilton syringe was employed to withdraw 30-μL samples from the absorber. These samples were withdrawn slowly and carefully in order to avoid desorption of hydrogen. They were then immediately injected into a Model 1420 (Varian Instrument Co.) chromatograph operated at conditions also shown in Table I. The calibration procedure in this case consisted of injecting into the chromatograph 30–150-μL samples of a gas mixture containing 5.00 ± 0.03% H_2 in nitrogen, using a 500-μL, gastight Hamilton syringe. The mixture was prepared by evacuating a steel vessel, originally flushed with nitrogen, to 2 mmHg. Then hydrogen was introduced until the pressure reached 14.7 psia. Finally, nitrogen was added to bring the pressure to 294 psia.

Results and Discussion

In the calibration procedure, the moles of hydrogen in the gas samples were calculated by supposing ideal-gas behavior at 25 °C and 1 atm. This assumption introduced less than 0.1% error. The calibration curve was obtained by plotting moles of hydrogen vs. the area of the response peak. It is estimated that the resulting curve could be in error by a maximum of 2%. Peak area values for the samples of liquid α-methylstyrene saturated with hydrogen were then compared with the calibration curves to establish the solubility.

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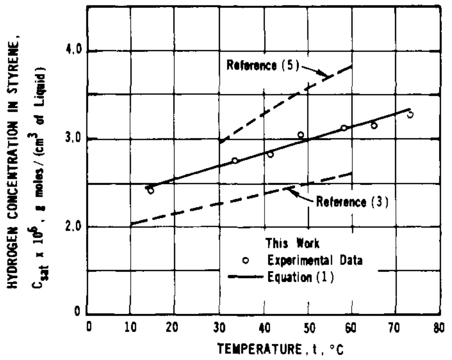

Figure 1. Solubility of hydrogen in α-methylstyrene at 1 atm pressure.

The experimental solubilities are summarized in Table II. The average of the four to six measurements at each temperature is plotted in Figure 1.

The points do not show a pronounced deviation from a linear solubility-temperature dependency. Assuming linearity, a straight-line relationship through the data points in Figure 1 was evaluated by minimizing the sum of the squares of the deviations. The relationship is

$$C_{sat} = (2.26 + 0.0145t) \times 10^{-6}, \text{g-mol/cm}^3 \quad (15 \leqslant t \leqslant 74\ ^\circ\text{C}) \qquad (1)$$

The standard deviation is 0.064×10^{-6} or about 3%.

A literature search revealed no experimental studies other than the two commonly quoted references (*3*, *5*). Solubility curves from these studies are also shown in Figure 1. The measurements of Polejes (*3*) covered the range 10–60 °C, while the Satterfield et al. data were for 30–60 °C. At low temperatures (~20 °C) all the results in Figure 1 agree within 15%, but at higher temperatures (~60 °C) the data from ref 3 and 5 differ by about 40%. The solubilities from our studies are between the results of the earlier work. It also should be mentioned that preliminary measurements in our laboratory, with less sensitive apparatus and less accurate technique, gave solubilities that were scattered, but within 10% of the final data. It has been mentioned (*6*) that a Ph.D. thesis of Jawad K. Ali (University of Birmingham, England, 1974) reported a maximum at 58 °C in the solubility vs. temperature curve for hydrogen in α-methylstyrene. Our results given in Figure 1 show no maximum in the range 15–74 °C.

Acknowledgment

The Dow Chemical Co. supplied α-methylstyrene.

Glossary

C_{sat}	concentration of hydrogen in α-methylstyrene in equilibrium with pure hydrogen gas at 25 °C and 1 atm pressure, g-mol/cm^3
t	temperature, °C

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Volumetric Properties of Molten Calcium and Cadmium Nitrate Tetrahydrates with Rubidium and Cesium Nitrates

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Densities of molten calcium and cadmium nitrate tetrahydrates containing rubidium and cesium nitrates were measured at temperatures ranging between 288.2 and 363.2 K. Densities and equivalent volumes varied linearly with temperature. Trends in equivalent volume–composition isotherms suggest that Rb^+ and Cs^+ ions do not compete for water of hydration bound with divalent cations.

Molten hydrated salts containing 4–6 mol of water/mol of salt have been considered as an analogue of molten salts (*1*) since the water of hydration remains strongly bound to cation giving weak field species of the type $M(H_2O)_n{}^{m+}$. Several alkaline earth metal nitrate hydrates–alkali metal nitrate mixtures show strong glass-forming and supercooling tendencies, enabling measurements well below the freezing points. In view of the recent interest in such systems (*1*, *2*, *4*, *6*), densities of molten calcium and cadmium nitrate tetrahydrates containing rubidium and cesium nitrates are reported in this paper.

Experimental Section

Calcium and cadmium nitrate tetrahydrates were Analar (BDH) grade; the water content of the salts, determined by volumetric titration using EDTA, were within ±0.01 of the stoichiometric value. Rubidium and cesium nitrate, extra pure (E. Merck), were dried to constant mass at 150 °C and stored over anhydrous magnesium perchlorate until used.

Details of the densitometer, calibration and precision in the acquisition of data, etc., have been described earlier (*8*). Data were obtained both in heating and cooling cycles at 5 °C interval.

Results and Discussion

Densities of several mixtures of calcium and cadmium nitrate tetrahydrates with rubidium and cesium nitrates, obtained at temperatures ranging between 288.2 and 363.2 K, are presented