Solubilities of Some Olefins in Aqueous Solutions

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Solubilities of some C_5–C_8 straight-chain and cyclic olefins in the range 15–40°C in aqueous acidic solutions have been determined analytically. The heats of solution have also been determined.

In the study of the interaction of metal salts with olefins in an aqueous medium, it was necessary to determine the solubilities of the olefins in acid solutions. The literature showed that such data are not available for many olefins. Only McAuliffe (*4*) has reported the solubilities of some olefins in water at 25°C by the use of the gas chromatograph method. In the present work are reported solubilities of some cyclic and straight-chain C_5–C_8 olefins in 0.001*M* HNO_3, 0.05*M* and 0.1*M* HCl, at several temperatures.

EXPERIMENTAL

Cyclohexene, cyclopentene, 2-hexene, 2-heptene, and 2-octene were prepared by the vapor-phase dehydration of the corresponding primary alcohols over alumina catalyst (prepared in the laboratory by precipitation with NH_4Cl from sodium aluminate) at 350–450°C (*3*). 2-Methyl-2-butene was prepared by the sulfuric acid dehydration of *t*-amyl alcohol (*6*). The olefins were washed with cold aqueous sodium carbonate, then with chilled water, and dried successively over calcium chloride and sodium metal and were fractionated. Constant-boiling fractions were collected. They were identified by infrared (ir) and proton magnetic resonance (pmr) spectra and tested for purity by gas liquid partition chromatography (glpc). These tests confirmed the identity of the olefins and their purity but 2-heptene and 2-octene were mixtures of cis and trans isomers in the ratio (trans/cis) 1.0 and 1.09 for 2-heptene and 2-octene, respectively. 1-Hexene, 1-heptene, and 1-octene were of Matheson, Coleman and Bell, USA grade (purity 99%) and 1-decene of BDH grade (purity 99%). The samples were tested for peroxides by the routine procedure (*5*) and if present, they were removed and distilled before use.

To obtain a saturated solution of the olefin in the required aqueous medium, the following procedure was adopted. The aqueous medium (15 ml) was shaken mechanically with 1 ml

Table I. Saturation Solubilities of Olefins at Several Temperatures in 0.001*M* HNO_3, 0.05*M* HCl, and 0.1*M* HCl and Heat of Solution Data

	Solubility of olefin (mol/l.) in					
Olefin	0.001*M* HNO_3 × 10^3	ΔH	0.05*M* HCl × 10^3	ΔH	0.1*M* HCl × 10^3	ΔH
Cyclohexene	4.95 ± 0.19[a] (30°C)[a]	−12.3	. . .		3.20 ± 0.18 (25°C)	−0.91
	3.46 ± 0.17 (35°C)				3.18 ± 0.19 (30°C)	
	2.49 ± 0.17 (40°C)				3.11 ± 0.22 (35°C)	
Cyclopentene	9.21 ± 0.23 (20°C)	−1.37	8.77 ± 0.28 (25°C)	−0.91	. . .	
	8.97 ± 0.23 (25°C)		8.62 ± 0.29 (30°C)			
	8.71 ± 0.26 (30°C)		8.48 ± 0.23 (35°C)			
2-Methyl-2-butene	5.15 ± 0.21 (15°C)	−2.51	. . .		4.31 ± 0.24 (15°C)	−1.37
	4.88 ± 0.16 (20°C)				4.19 ± 0.16 (20°C)	
	4.61 ± 0.20 (25°C)				4.01 ± 0.18 (25°C)	
2-Hexene	0.875 ± 0.021 (20°C)	−7.77	0.716 ± 0.021 (25°C)	−7.77	. . .	
	0.799 ± 0.023 (25°C)		0.606 ± 0.023 (30°C)			
	0.660 ± 0.026 (30°C)		0.511 ± 0.021 (35°C)			
2-Heptene	0.340 ± 0.018 (15°C)	−5.03	0.206 ± 0.015 (25°C)	−3.66	. . .	
	0.321 ± 0.014 (20°C)		0.187 ± 0.015 (30°C)			
	0.271 ± 0.015 (25°C)		0.166 ± 0.018 (35°C)			
2-Octene	0.292 ± 0.014 (15°C)	−5.94	0.184 ± 0.014 (25°C)	−5.49	. . .	
	0.251 ± 0.016 (20°C)		0.160 ± 0.015 (30°C)			
	0.216 ± 0.015 (25°C)		0.139 ± 0.015 (35°C)			
1-Hexene	0.778 ± 0.023 (25°C)	−8.46	. . .		. . .	
	0.643 ± 0.028 (30°C)					
	0.501 ± 0.021 (35°C)					
1-Heptene	0.316 ± 0.013 (20°C)	−5.49	. . .		. . .	
	0.281 ± 0.012 (25°C)					
	0.245 ± 0.015 (30°C)					
1-Octene	0.239 ± 0.011 (20°C)	−8.69	. . .		. . .	
	0.197 ± 0.014 (25°C)					
	0.153 ± 0.016 (30°C)					
1-Decene	0.082 ± 0.003 (15°C)	−10.98	. . .		. . .	
	0.061 ± 0.004 (20°C)					
	0.041 ± 0.004 (25°C)					

ΔH reported here is in kcal/mol.
[a] Standard deviation from mean.

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Table II. Comparison of Solubility Data for Some Olefins

Olefin	Lit. data, mol/l.[a]	Present work, mol/l.[b]
Cyclopentene	0.008678 (590)	0.008978
Cyclohexene	0.002743 (225)	0.004950[c]
1-Hexene	0.0005952 (50)	0.0007781
2-Heptene	0.0001530 (15)	0.0002716
1-Octene	0.00002142 (2.4)[d]	0.0001979

[a] Determined by gas chromatography (*4*) at 25 ± 1.5°C. The quantities in parentheses are reported solubilities in grams per 10^6 grams of water. The quantity reported here is calculated from this value. [b] Determined at 25°C by the electrometric bromine number method. [c] The value reported is at 30°C. [d] The value reported by the worker is doubted.

of olefin in a pyrex-jacketed buret at a given temperature and allowed to equilibrate at the same temperature. The temperature required both before shaking and during equilibration was obtained by circulating water through the jacket from an Ultrathermostat-type NBE (M/s Prufgerate Works, Medingen, Germany) which allowed the temperature to be maintained within ±0.05°C. There was no measurable change in the volume delivered by the buret for temperature variations of the order of 20°C from room temperature. After the aqueous phase showed the absence of olefin globules, as judged visually, 5 ml of the aqueous layer was withdrawn and the olefin content determined by the value of the bromine number using the dead-stop electrometric titration technique (*2*) with some minor modifications. This modification was in the composition of the titration solvent and was altered to prevent carbon tetrachloride from being separated on introduction of the aqueous phase. The final composition chosen by trial and error was 2000 ml of glacial acetic acid (BDH), 200 ml of carbon tetrachloride (distilled), 110 ml of methanol (BDH, acetone free), and 18 ml of 1:5 sulfuric acid (BDH, AR). The solubilities reported are the average of a minimum of four determinations.

RESULTS

The solubilities of the olefins in the respective mediums are reported in Table I. The trends in the data are in the expected direction, considering the increase in the ionic strength of the medium [increasing ionic strength, lower solubility (*1*)]; ΔH for the solubilities are determined from a plot of log (solubility) vs. reciprocal absolute temperature and are recorded in the same table. Furthermore, the logarithm of the solubility in water is a linear function of the hydrocarbon molar volume (Figure 1), in accordance with the observation made earlier (*4*). Table II compares previously reported data for solubilities in water with those determined in the present work. The values are of the same order of magnitude.

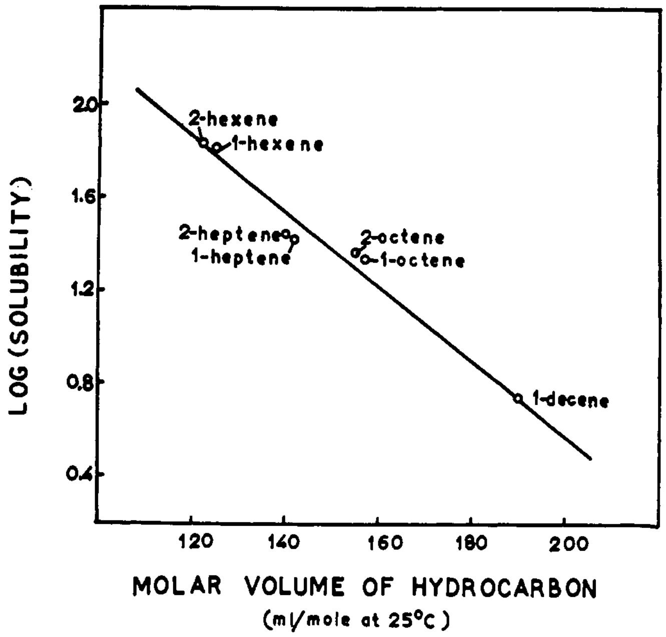

Figure 1. Solubility in water (0.001M HNO_3) of olefin hydrocarbons as function of their molar volumes at 25°C

Solubility in grams/10^6 grams of water

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