

Figure 4. Vaporization equilibrium ratio of *n*-decane in $H_2 + n$ -decane.

Hydrogen gas was supplied by Airco with a purity of 99.95%. Gold label grade *n*-decane was purchased from the Aldrich Chemical Co. with a reported purity of 99+%.

Samples of the condensates from both the overhead and bottom cell effluents were collected at each experimental condition. The condensates were analyzed on a Chicago Nuclear gas chromatograph and no decomposition products were found at any of the conditions studied. Nevertheless, *n*-decane recovered from the cell effluents was fractionally distilled under a reduced nitrogen atmosphere before being reused.

The fluctuation of the equilibrium cell temperatures was less than 0.2 °C during the measurement of all of the points on an isotherm.

Results

Figure 1 shows the mole fraction of hydrogen in the liquid

phase at four temperatures between 189 and 310 °C. Data were taken at seven pressures between 20 and 250 atm at each temperature except for the highest temperature, 310 °C, where data were taken at only five pressures from 50 to 250 atm. Excessive vaporization of *n*-decane at the lower pressures and highest temperature made it impossible to take accurate data. The isothermal solubilities extrapolate smoothly to $x_H = 0$ at the vapor pressure of *n*-decane. The vapor pressure of *n*-decane is taken from ref 4. The saturated vapor compositions are shown in Figure 2. At each set of temperature and pressure conditions at least two samples of both the overhead and bottoms were taken. The agreement among replicate points was, in general, within 1% in mole fraction of hydrogen. The individual data points are shown in Figures 1 and 2 when they can be distinguished. The average values of the replicate samples are reported in Table I. These average values of x_H and y_H were used to calculate the equilibrium ratios which are also reported in Table I and shown respectively in Figures 3 and 4 for hydrogen and *n*-decane.

Glossary

K	vaporization equilibrium ratio, $K = y/x$
p	pressure, atm
t	temperature, °C
x	mole fraction in the liquid phase
y	mole fraction in the gas phase

Subscripts

D	<i>n</i> -decane
H	hydrogen

Literature Cited

- (1) Simnick, J. J., Lawson, C. C., Lin, H. M., Chao, K. C., *AIChE J.*, **23**, 469 (1977).
- (2) Simnick, J. J., Liu, K. D., Lin, H. M., Chao, K. C., *Ind. Eng. Chem. Process Des. Develop.*, **17**, 204 (1978).
- (3) Simnick, J. J., Sebastian, H. M., Lin, H. M., Chao, K. C., *J. Chem. Thermodyn.*, **11**, 531 (1979).
- (4) Zwolinski, B. J., Ed., "Selected Values of Properties of Hydrocarbons and Related Compounds", A.P.I. Research Project 44, Thermodynamics Research Center, Texas A&M University, 1976.

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Excess Enthalpies for Mixtures of Acetonitrile and Aromatic Hydrocarbons

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Measurements of excess enthalpies were carried out at 25 and 41.2 °C for binary mixtures of acetonitrile with benzene, toluene, ethylbenzene, *p*-xylene, and *m*-xylene.

This paper is part of an experimental investigation of the thermodynamic excess functions of binary mixtures consisting of an aromatic hydrocarbon and acetonitrile. This paper reports excess enthalpies for these systems.

Table I. Excess Enthalpy Data for Benzene-Acetonitrile Mixtures

$T = 25\text{ }^{\circ}\text{C}$		$T = 41.2\text{ }^{\circ}\text{C}$	
x_1	H^E , cal/mol	x_1	H^E , cal/mol
0.0420	24.4	0.0645	35.9
0.0855	46.6	0.1370	66.2
0.1330	66.3	0.2190	90.0
0.1850	83.0	0.3150	108.0
0.2415	96.6	0.3580	112.5
0.2705	103.0	0.4170	114.2
0.3120	107.0	0.4610	115.1
0.3470	109.6	0.5070	113.0
0.3570	108.6	0.5570	109.9
0.3955	109.9	0.6100	105.1
0.4360	109.9	0.6670	97.3
0.4950	107.3	0.8260	61.2
0.5790	97.5		
0.6610	86.1		
0.7620	66.2		
0.8800	38.2		

Table II. Excess Enthalpy Data for Toluene-Acetonitrile Mixtures

$T = 25\text{ }^{\circ}\text{C}$		$T = 41.2\text{ }^{\circ}\text{C}$	
x_1	H^E , cal/mol	x_1	H^E , cal/mol
0.0540	36.2	0.1115	68.2
0.1130	67.8	0.1740	95.2
0.1810	94.2	0.2450	115.8
0.2250	107.0	0.2960	126.0
0.2700	117.2	0.3280	130.8
0.3030	122.5	0.3350	135.8
0.3220	124.6	0.3540	138.0
0.3370	127.0	0.3930	141.2
0.3600	128.0	0.4360	143.1
0.4000	129.8	0.4820	142.8
0.4420	129.5	0.5300	140.6
0.5100	126.0	0.5810	136.0
0.6370	108.0	0.7190	112.0
0.7840	72.5	0.8650	67.6
0.9680	14.9		

Table III. Excess Enthalpy Data for Ethylbenzene-Acetonitrile Mixtures

$T = 25\text{ }^{\circ}\text{C}$		$T = 41.2\text{ }^{\circ}\text{C}$	
x_1	H^E , cal/mol	x_1	H^E , cal/mol
0.0430	36.6	0.0418	37.0
0.0895	69.5	0.0885	70.4
0.1425	98.2	0.1400	99.5
0.1810	114.7	0.1980	124.0
0.2230	128.7	0.2620	142.3
0.2690	139.8	0.2970	153.2
0.2920	144.0	0.3040	151.0
0.2990	147.2	0.3290	158.7
0.3075	146.3	0.4010	164.8
0.3265	151.3	0.4400	165.0
0.3735	155.5	0.4820	163.3
0.4385	156.4	0.5250	159.5
0.5100	151.8	0.5720	153.2
0.5910	140.5	0.7010	125.0
0.6800	121.2	0.8480	75.6
0.8310	74.2		

To our knowledge, data of excess enthalpies are available in the literature only for the benzene-acetonitrile system (1).

In this study, besides benzene we also considered toluene, ethylbenzene, *p*-xylene, and *m*-xylene.

Experimental Section

Measurements of excess enthalpy were made in an LKB adiabatic calorimeter (Model 8700). Data were obtained for all the systems at 25 and $41.2 \pm 1\text{ }^{\circ}\text{C}$. Care was taken to reduce the vapor space, so vaporization and heat corrections were not applied. Resulting errors are within the uncertainties in the

Table IV. Excess Enthalpy Data for *p*-Xylene-Acetonitrile Mixtures

$T = 25\text{ }^{\circ}\text{C}$		$T = 41.2\text{ }^{\circ}\text{C}$	
x_1	H^E , cal/mol	x_1	H^E , cal/mol
0.0182	15.1	0.0865	70.3
0.0620	50.3	0.1355	99.7
0.1105	81.8	0.1885	124.8
0.1640	108.8	0.2460	144.8
0.2110	127.2	0.2870	155.2
0.2480	138.5	0.3080	160.8
0.2735	144.8	0.3260	164.0
0.2980	150.0	0.3620	169.0
0.3040	152.0	0.4010	173.0
0.3380	157.8	0.4420	174.8
0.3760	161.8	0.4850	174.2
0.4150	163.8	0.6030	162.4
0.4580	164.1	0.7300	131.2
0.5740	154.0	0.8650	77.8
0.7060	126.5		
0.8540	76.5		

Table V. Excess Enthalpy Data for *m*-Xylene-Acetonitrile Mixtures

$T = 25\text{ }^{\circ}\text{C}$		$T = 41.2\text{ }^{\circ}\text{C}$	
x_1	H^E , cal/mol	x_1	H^E , cal/mol
0.0593	43.2	0.0820	70.4
0.1040	75.5	0.1290	100.2
0.1535	103.8	0.1795	126.8
0.2080	127.3	0.2350	146.9
0.2420	139.0	0.2940	162.5
0.2670	146.0	0.3060	169.5
0.2830	151.0	0.3220	172.5
0.2920	152.0	0.3910	181.3
0.3120	155.3	0.4280	183.5
0.3180	156.8	0.4680	184.0
0.3430	159.0	0.5100	182.0
0.3920	160.8	0.6220	166.5
0.4260	159.8	0.7450	133.0
0.5200	148.5	0.8750	78.2
0.6620	118.0		
0.8300	74.1		

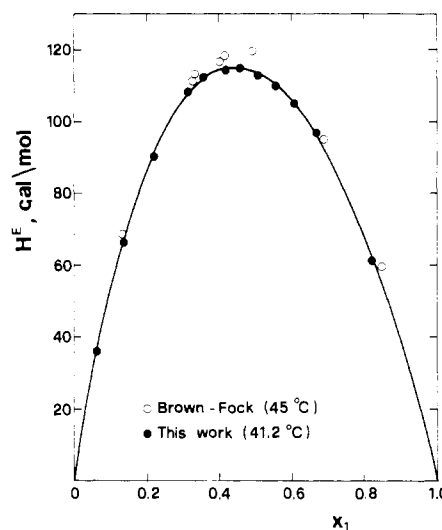


Figure 1. Excess enthalpies of the benzene (1)-acetonitrile (2) system at $41.2\text{ }^{\circ}\text{C}$. The curve is the least-squares representation of data by eq 1.

temperature measurements. The details of the experimental procedure are reported elsewhere (2, 3).

Carlo Erba analytical grade materials were used without further purification. Refractive indexes of the samples used for the measurements are as follows at $20\text{ }^{\circ}\text{C}$: benzene, 1.5011; toluene, 1.4961; ethylbenzene, 1.4959; *p*-xylene, 1.4958; *m*-xylene, 1.4973; acetonitrile, 1.3430.

Table VI. Values of the Constants and Standard Deviations^a (cal/mol) for the Representation of Excess Enthalpies by Equation 1

	benzene		toluene		ethylbenzene		p-xylene		m-xylene	
	25 °C	41.2 °C	25 °C	41.2 °C	25 °C	41.2 °C	25 °C	41.2 °C	25 °C	41.2 °C
A	429.2	455.4	503.8	567.8	604.7	641.8	650.6	690.2	635.0	726.4
B	-147.9	-90.5	-142.6	-67.9	-188.5	-165.9	-132.8	-121.8	-214.2	-119.1
C	63.8	76.0	106.6	110.0	127.6	136.4	103.5	132.8	0.3	141.8
σ	0.591	0.212	0.985	0.134	0.377	0.292	0.247	0.850	1.595	0.112

$$^a \sigma = [\sum_1^n (H^E_{\text{calcd}} - H^E_{\text{exptl}})_i^2 / (n - 1)]^{1/2}.$$

Discussion

The experimental results are listed in Tables I-V. The excess enthalpy is positive in the whole range of composition, for all the systems. It can be observed that the maximum of excess enthalpy increases with the temperature and the number of carbon atoms of the hydrocarbon.

Data were correlated by means of the Redlich and Kister equation

$$H^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2] \quad (1)$$

where x_1 and x_2 are the mole fractions of hydrocarbon and acetonitrile. Values of the constants obtained by the least-squares method are summarized in Table VI, along with the standard deviations.

The results obtained for the benzene-acetonitrile system at 41.2 °C are compared with Brown and Fock's data at 45 °C in Figure 1. The agreement is good if one considers the difference of temperatures.

Literature Cited

- (1) Brown, I., Fock, W., *Aust. J. Chem.*, **9**, 180 (1956).
- (2) Di Cave, S., Chianese, A., Prantero, A., *J. Chem. Eng. Data*, **23**, 279 (1978).
- (3) Sunner, S., Wadso, S., *Sci. Tools*, **13**, 1 (1966).

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Physical Properties of Water in Fuel Oil Emulsions (Density and Bulk Compressibility)

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The densities and bulk compressibilities of pure fuel oils and of ultrasonically formed water in fuel oil emulsions are reported as a function of the volume fraction of water contained in the emulsion at several temperatures. The fuel oils investigated were regular leaded gasoline, no. 2 diesel fuel, no. 4 heating oil, and no. 6 fuel oil. Volume fractions of water in emulsions varied from 0.001 to 0.100. The density of water in regular leaded gasoline emulsions was measured at 0 and 30 °C while the densities of water in no. 2 diesel fuel emulsions, water in no. 4 heating oil emulsions, and water in no. 6 fuel oil emulsions were measured at 30 and 60 °C. Bulk compressibilities were determined at 0 °C for water in gasoline emulsions, 30 °C for water in no. 2 diesel fuel emulsions, 30 and 70 °C for water in no. 4 heating oil emulsions, and 50 °C for water in no. 6 fuel oil emulsions. Both the density and compressibility measurements were found to be reproducible. Equations describing the variation of density and compressibility of these emulsions with temperature and volume fraction of water are presented.

Introduction

In recent years there has been a growing interest in the application of water in fuel oil emulsions to pollution abatement and fuel conservation. It has been found that the use of water in fuel oil emulsions results in fuel savings and reduced particulate

and NO emissions.¹ Use of water in fuel oil emulsions also increases thermal efficiency in a boiler. This study of the densities and compressibilities of water in fuel oil emulsions was performed to provide a reliable data base for use in the design of emulsion combustion systems.

Experimental Section

A. Density. The fuel oils used in this study of water in fuel oil emulsions were regular leaded gasoline, no. 2 diesel fuel, no. 4 heating oil, and no. 6 fuel oil. The water used in the emulsions was double distilled to ensure purity.

In a previous report,² the density, viscosity, and interfacial tension against water for the four fuel oils to be emulsified were found to decrease linearly with increasing temperature. The viscosities were found to decrease exponentially with increasing temperature. The stability of octacosane and of hexatriacontane in water was also studied and was characterized as a function of particle size and particle size distribution. Stabilities of water in gasoline and water in no. 2 diesel fuel were determined by measuring the amount of water creamed out. They were found to be unstable because they breakdown within 10 min. Stabilities of water in no. 4 heating oil and water in no. 6 fuel oil were determined by measuring viscosity as a function of time. They were found to be stable for at least an hour at room temperature. Viscosities of water in oil emulsions were found to increase linearly with increase in water fraction. Densities of water in oil emulsions were also measured. They, too, were found to