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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] $\sigma = [\Sigma_1^n(H^E_{calcd} - H^E_{exptl})_i^2/(n-1)]^{1/2}$.

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

$$H^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2] \qquad (1)$$

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.

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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

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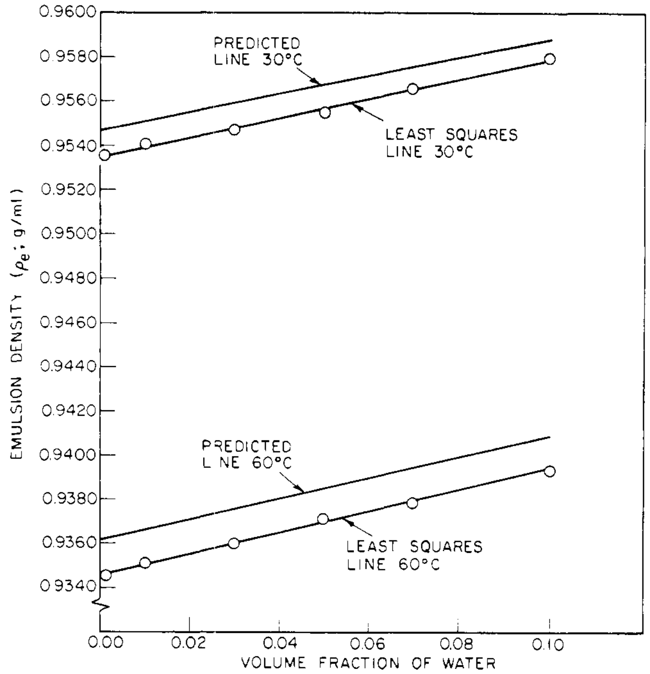

Figure 1. Density of emulsions of water in no. 6 fuel oil vs. volume fraction of water.

increase linearly with increase in water fraction.

The densities were determined by using a Weld-type pycnometer. The pycnometer volume was determined by using water at 30 °C (ρ = 0.995 646).[3] The clean, dry pycnometer was filled with fuel oil (or water/oil emulsion), capped, and placed in a water bath. Temperature equilibration took 2–4 min, depending on the sample. After equilibration, the liquid level in the pycnometer neck was adjusted to the fiducial mark (to the top of the neck with no. 6 fuel oil) with filter paper. The pycnometer was removed, its exterior was dried, and it was weighed (Right-A-Weigh, Ainsworth and Sons, Inc.). At least three weights were recorded for each data point. The net weights of the samples were corrected to account for buoyancy effects. The average weight was then divided by the pycnometer volume to determine the density of the sample.

B. Compressibility. The compressibilities of the pure oils and the emulsions were determined from the equation

$$\beta = 1/\rho c^2 \tag{1}$$

where β = bulk compressibility, 1/Pa, ρ = density, kg/m^3, and c = speed of sound in sample, m/s. The densities used in eq 1 were those previously determined. The speed of sound in a sample was determined by using a Branson Sonoray Series 600 ultrasonic tester. A sample of oil or emulsion was placed in a jacketed tube with a flat metal bottom. Water was circulated from a water bath through the jacket to maintain the sample at a constant temperature. After temperature equilibration, the Sonoray probe was partially immersed in the sample. The cathode ray tube output was photographed to allow for accurate measurement with calipers. Photographs of water and acetone were taken as calibration for the water in oil emulsion measurements.

Discussion of Results

A. Density. The density of pure gasoline was measured at 10 °C intervals from 20 to 40 °C, while the density of pure no. 2 diesel fuel was measured at 10 °C intervals from 20 to 90 °C. The densities of pure no. 4 heating oil and pure no. 6 fuel oil were measured at 20 °C intervals from 20 to 80 °C.[2] For each fuel a linear least-squares analysis was performed on each data set and showed an equation of the form $\rho = AT + B$ adequately described the variation of density with temperature. Here ρ is density, T is temperature (°C), and A and B are constants. Results are shown in Table I.

Table I. Temperature Effect on Density of Fuel Oils by Least-Squares Analysis ($\rho = AT + B$)

fuel	10^4A, g mL^{-1} °C^{-1}	B, g/mL	corrlatn coeff	std error
gasoline	−7.750	0.7494	−0.9997	0.0001
no. 2 oil	−6.756	0.8702	−0.9999	0.0002
no. 4 oil	−6.320	0.9155	−0.9999	0.0002
no. 6 oil	−6.165	0.9732	−0.9998	0.0002

Table II. Emulsion Density Least-Squares Characteristics ($\rho = A\phi_w + B$)

fuel	temp, °C	A, g mL^{-1}	B, g/mL	corrlatn coeff	std error
gasoline	0	0.2766	0.7510	0.9912	0.0004
gasoline	30	0.2536	0.7263	0.9985	0.0001
no. 2 oil	30	0.1331	0.8489	0.9972	0.0003
no. 2 oil	60	0.1208	0.8302	0.9956	0.0004
no. 4 oil	30	0.1180	0.8956	0.9931	0.0005
no. 4 oil	60	0.1043	0.8782	0.9943	0.0004
no. 6 oil[a]	30	0.0438	0.9535	0.9961	0.0001
no. 6 oil[a]	60	0.0476	0.9346	0.9992	0.0001

[a] See Figure 1 for graphical representation.

Table III. Emulsion Density Predicted Values of Least-Squares Constants ($\rho = A\phi_w + B$)

fuel	temp, °C	A, g/mL	B, g/mL
gasoline	0	0.2504	0.7494
gasoline	30	0.2694	0.7262
no. 2 oil	30	0.1456	0.8500
no. 2 oil	60	0.1535	0.8298
no. 4 oil	30	0.0991	0.8965
no. 4 oil	60	0.1057	0.8776
no. 6 oil[a]	30	0.0409	0.9547
no. 6 oil[a]	60	0.0470	0.9362

[a] See Figure 1 for graphical representation.

The densities of water in no. 2 diesel fuel, water in no. 4 heating oil, and water in no. 6 fuel oil emulsions were measured at 30 and 60 °C. The volume fraction of water (ϕ_w) contained in these emulsions ranged from ϕ_w = 0.001 to ϕ_w = 0.100. Owing to problems with evaporation and creaming, water in gasoline emulsion densities were measured at 0 and 30 °C over a range of ϕ_w = 0.001 to ϕ_w = 0.070.[2]

For each fuel oil, a plot of density as a function of volume fraction of water was made. A linear least-squares analysis was performed on each line, generating an equation of the form $\rho_e = A\phi_w + B$. The results are shown in Table II. In all cases, the correlation coefficient was very close to ±1. This indicates that the data are described very well by the corresponding equation. The small values of the standard error of estimate indicate good reproducibility of results.

If no change in volume occurs due to the mixing of water and fuel oil, the density of the emulsion would be represented by

$$\rho_e = \rho_w\phi_w + \rho_o(1 - \phi_w) \tag{2}$$

Upon rearrangement

$$\rho_e = (\rho_w - \rho_o)\phi_w + \rho_o \tag{3}$$

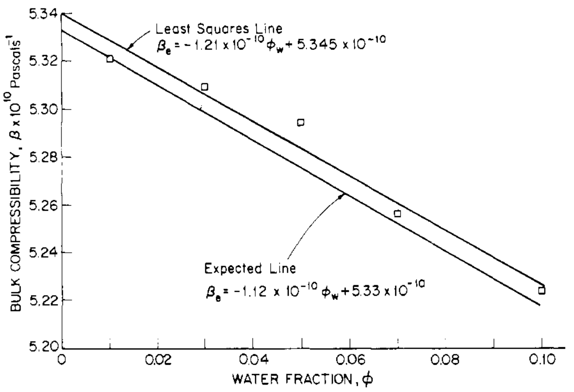

Figure 2. Bulk compressibility of emulsions of water in no. 6 fuel oil vs. volume fraction of water at 50 °C.

where ϕ_w = volume fraction of water, ρ_e = density of emulsion, ρ_w = density of water, and ρ_o = density of oil.

One observes that the emulsion density varies linearly with volume fraction water and with temperature. Equations predicting emulsion densities as functions of the volume fraction water were determined by using previously measured fuel oil densities and known water densities. These equations are shown in Table III.

Comparison of the densities determined from the experimental data never differed by more than half of 1% from the emulsion densities predicted by Table III equations over the range of ϕ_w studied. This suggests that there was no volume change during emulsification and that the small variations were due to experimental error and creaming.

B. Compressibility. The bulk compressibilities for water in no. 2 diesel fuel emulsions, water in no. 4 heating oil emulsions, and water in no. 6 fuel oil emulsions were determined at 30 °C over the range $\phi_w = 0.001$ to $\phi_w = 0.100$. Owing to the high volatility of gasoline, the compressibilities of water in gasoline emulsions were measured primarily at 0 °C over the same range of ϕ_w. The water in no. 4 heating oil emulsion was also investigated at 70 °C to determine the effect of temperature on bulk compressibility. Compressibilities of the pure oils were also determined.[4] In all cases a plot of bulk compressibility of emulsion (β_e) as a function of volume fraction of water (ϕ_w) was constructed. (A linear least-squares analysis was carried out and an equation of the form $\beta_e = A\phi_w + B$ was found to describe the data very well.) The results are shown in Table IV. In all cases the correlation coefficient was in the range of 1 ± 0.11 indicating fairly reasonable agreement with the above equation. The small values of the standard error of estimate indicate good reproducibility. If no change in compressibility occurs (due to the mixing of the water and fuel oil), the compressibility of the emulsion should be represented by

$$\beta_e = \beta_w\phi_w + \beta_o(1 - \phi_w)$$

Upon rearrangement

$$\beta_e = (\beta_w - \beta_o)\phi_w + \beta_o$$

Table IV. Least-Squares Characteristics of Equations for the Bulk Compressibility Where $\beta_e = A\phi_w + B$

fuel	temp, °C	$10^{10}A$, Pa^{-1}	$10^{10}B$, Pa^{-1}	corrlatn coeff	std error × 10^{10}
gasoline	0	−2.32	7.90	0.8922	0.1833
no. 2 oil	30	−1.856	6.270	0.9687	0.0353
no. 4 oil	30	−1.55	5.637	0.9876	0.0125
no. 4 oil	70	−3.42	6.756	0.8999	0.0576
no. 6 oil[a]	50	−1.12	5.338	0.9835	0.0071

[a] See Figure 2 for graphical representation.

Table V. Predicted Values for the Coefficients A and B in the Equation $\beta_e = A\phi_w + B$ for the Bulk Compressibility of Fuel Oils

fuel	temp, °C	$10^{10}A$, Pa^{-1}	$10^{10}B$, Pa^{-1}
gasoline	0	−2.32	7.90
no. 2 oil	30	−1.86	6.27
no. 4 oil	30	−1.23	5.623
no. 4 oil	70	−2.692	6.662
no. 6 oil[a]	50	−1.21	5.345

[a] See Figure 2 for graphical representation.

where β_e = bulk compressibility of emulsion, β_w = bulk compressibility of water, β_o = bulk compressibility of oil, and ϕ_w = volume fraction of water. Equations predicting emulsion compressibilities as a function of the volume fraction of water were determined by using previously measured fuel oil compressibilities and known water compressibilities. The equations are shown in Table V. The compressibilities determined from the data never differed by more than half of 1% from the emulsion compressibilities predicted by Table V. This suggests that the compressibilities did not change upon mixing and that the small variations were due to experimental error and creaming.

Conclusions

The densities of emulsions of water in fuel oils were found to vary linearly with the volume fraction of water and with temperature. The compressibilities of emulsions of water in fuel oils were also found to vary linearly with the volume fraction of water.

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