Densities of Soybean Oil/Solvent Mixtures

P. Rice and W. Hamm
Department of Chemical Engineering, Loughborough University of Technology, Loughborough Leicestershire, LE11 3TU

Density data for soybean oil/acetone and soybean oil/n-hexane mixtures were measured at 20, 30 and 40 C using a PAAR DMA digital readout calculating precision density meter over the complete range of concentrations. When plotted as molar volume versus molar concentration the mixtures exhibited near ideal linear behavior. To check whether other oil/solvent mixtures behaved in a similar way, data from published literature were replotted in this form and the near ideal linear behavior was observed.

Using the data at 20 C, the excess volumes V^E were calculated, from which partial molar volumes for each component were obtained. These showed only slight variation over the composition range, confirming the near ideal behavior of these systems. Therefore, if densities of pure oil and solvent are known, their mixture density can be calculated by linear interpolation with sufficient accuracy for engineering design calculations.

With the use of solvent extraction in the edible oil industry and low temperature solvent crystallization there is need for accurate property data for the design of process equipment. We report accurate density measurements for soybean oil/acetone and soybean oil/n-hexane at 20, 30 and 40 C.

Data for 11 oil/solvent mixtures have been reported in the literature (1-5). One of these mixtures was soybean oil/n-hexane, and measurements were made at 25, 37.5 and 50 C. A comparison of soybean oil density variation with temperature with this data is shown in Figure 1. A straight line $\varrho = 0.933 - 0.000636T$ gave a linear regression correlation coefficient of 0.991 for the six data points, where ϱ is the density (g/ml) and T is the temperature (C). The agreement was satisfactory. Unfortunately the n-hexane used in their measurements was a commercial grade "Skellysolve B" so that no direct comparison of density can be made for this solvent. However, we have included a comparison of the density variation with composition for their measurements at 37.5 and ours at 40 C in Figure 2. One can see that the agreement is good with the biggest discrepancy for the solvents.

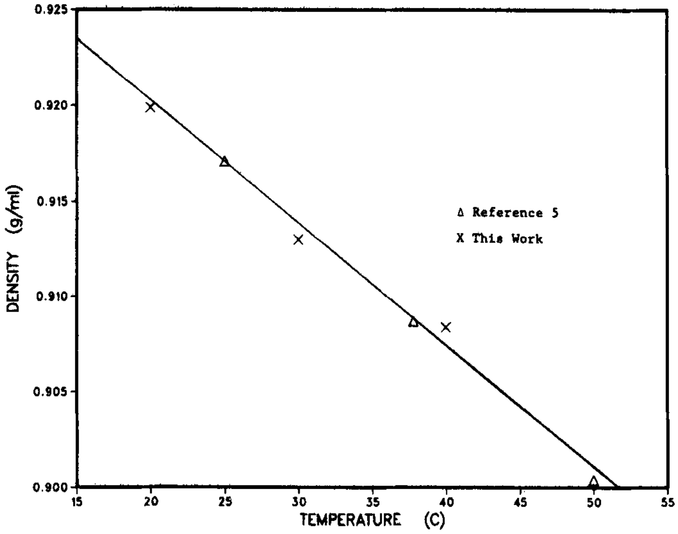

FIG. 1. Variations in density of soybean oil due to temperature.

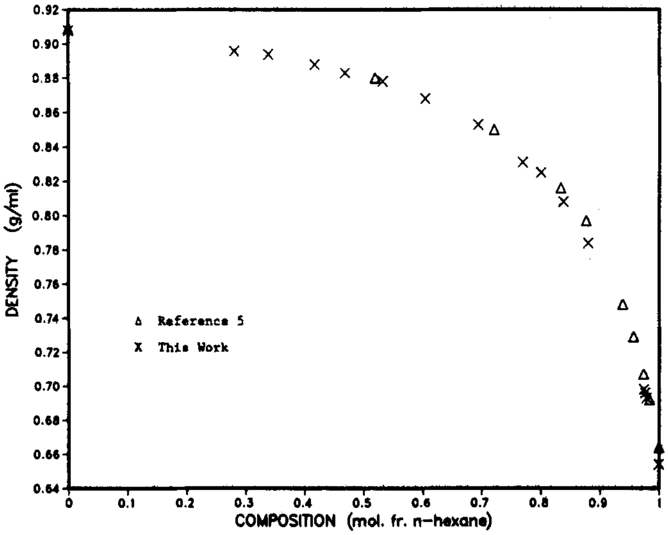

FIG. 2. Density changes with composition of soybean oil/n-hexane mixtures.

EXPERIMENTAL

Density measurements were made with a PAAR DNA digital readout calculating precision density meter, which operates on the basis of the oscillating tube principle developed by Kratky et al. (6). The density, ϱ, of a sample is calculated by the DNA according to the equation

$$\varrho = \frac{1}{A}(T^2 - B)$$

where T is the period of oscillation and A and B are apparatus constants which are determined for each experimental temperature by calculation using air and distilled water (deionized) as references. The density of water was taken from Le Neindre and Voder (7). The temperature within the sample tube was controlled to ± 0.1 C with a Heto type 04PT623 temperature controller and circulator bath which maintained the temperature at 20, 30 and 40 C required for the tests.

Solvents were research grade acetone and n-hexane, used without further treatment, purchased from Fisons plc, Loughborough, England.

The soybean oil was supplied by Unilever plc with a fatty acid methyl ester analysis of

14:0	16:0	16:1	18:0	18:1	18:2	18:3	20.0	20.1
Trace	10.3	Trace	4.0	22.6	54.4	8.0	0.5	-

The mean molecular weight of the soybean oil was calculated to be 873.

RESULTS AND DISCUSSION

Skau and coworkers (1-4) presented data for oil solvent mixtures in the form specific volume (g/ml) vs composition (weight fraction). This gave moderate negative deviations from ideal linear behavior, indicating contraction on mixing.

We have presented our data (Tables 1 and 2) in the form of density (g/ml) vs molar composition. However, we plotted the data in the form of molar volume vs composition (molar fraction). This indicated nearly ideal behavior (Fig. 3) that is $V_i = X_1V_1 + X_2V_2$. The correlation coefficient for the soy/acetone system was 0.999 and for the soy/n-hexane system 0.996, where the correlation coefficient was defined as:

$$\sqrt{\frac{\Sigma (X-\bar{X})\,(V-\bar{V})}{\Sigma (X-\bar{X})^2\, \Sigma (V-\bar{V})^2}}$$

and X and V are the mean values of composition and molar volume, respectively. This ideal behavior was also observed for acetone, a more polar solvent. We have reworked some of the data of Skau et al. for which we could estimate the mean molecular weight of the oil. The data showed near-ideal linear behavior even for the strongly polar solvents they used.

To demonstrate further near ideal behavior, excess volume defined as

$$V^E = V_e - (X_1V_1 + X_2V_2)$$

was calculated for the data at 20 C. Here, V_e is the experimentally determined molar volume of the mixture, V_1 and V_2 are the experimentally determined molar volumes of the oil and solvent and X_1 and X_2 are the molar compositions of the oil and solvent in the mixture (where $X_2 = 1 - X_1$). V^E represents the volume change on mixing so that the volume of the mixture is

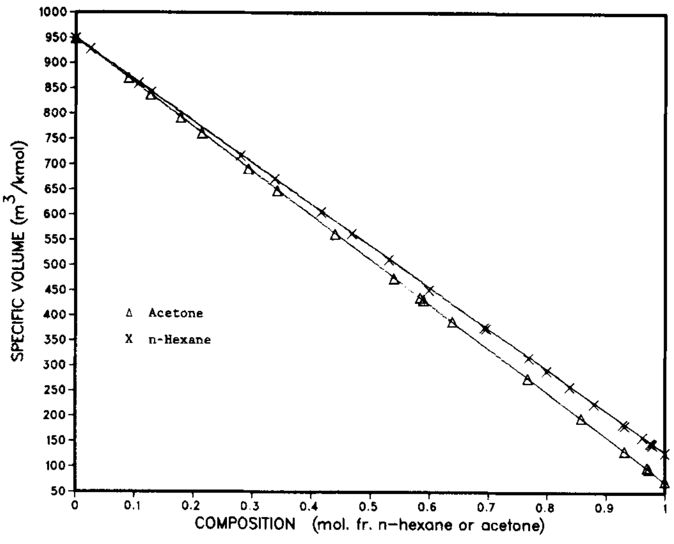

FIG. 3. Specific volume vs composition at 20 C for soybean with n-hexane and with acetone.

TABLE 1

Densities of Acetone/Soybean Versus Composition at 20, 30 and 40 C

Concentration (acetone) (mol fraction)	Density (g/ml)			Partial molar volume at 20 C (cm^3/mol)	
	20 C	30 C	40 C	$\tilde{V}_1$	$\tilde{V}_2$
0	.91990	.91297	.90841		949.016
.0902	.91890	.91225	-	74.258	949.237
.1272	.91860	.91185	-	74.045	949.249
.1793	.91774	.91114	-	73.724	949.213
.2147	.91825	.91000	-	73.523	949.163
.2937	.91618	.90953	.90449	73.192	949.006
.3435	.91500	.90697	.90214	73.084	948.898
.4410	.91270	.90583	.90086	73.082	948.740
.5416	.90921	.90116	.89646	73.264	948.737
.5847	.90773	.90054	.89550	73.359	948.794
.5909	.90717	.90039	.89504	73.372	948.804
.6396	.90424	.89430	.88562	73.461	948.902
.7681	.89417	.88263	.887756	73.517	949.048
.8588	.87836	.87048	.86035	73.386	948.577
.9319	.85545	.85373	.84683	73.303	947.381
.9695	.82848			73.35	946.339
.9731	.82454	.81253	.80397	73.36	946.221
1.0	.79003	.78024	.76880	73.478	

TABLE 2

Densities of n-Hexane/Soybean Versus Composition at 20, 30 and 40 C

Concentration (n-acetone) (mol fraction)	Density (g/ml)			Partial molar volume at 20 C (cm^3/mol)	
	20 C	30 C	40 C	$\tilde{V}_1$	$\tilde{V}_2$
0	.91990	.91297	.90841		949.016
.0251	.91894	.91233	-	118.507	949.624
.1072	.91583	.90948	-	120.392	949.455
.1279	.91536	.90874	-	120.657	949.190
.2803	.90792	.90137	.89652	123.069	949.636
.3379	.90491	.89840	.89353	124.774	947.582
.4170	.89994	.89307	.88817	125.941	947.702
.4685	.89547	.88863	.88375	126.884	947.952
.5320	.88960	.88312	.87839	127.809	948.311
.6044	.88049	.87370	.86864	128.468	948.610
.6940	.86553	.85865	.85324	128.617	948.286
.6972	.86448			128.607	948.249
.7688	.84406	.83684	.83157	128.114	946.686
.8005	.83741	.83042	.82485	127.748	945.432
.8386	.82208	.81419	.80848	127.241	943.352
.8798	.80087	.79283	.78461	126.734	940.400
.9294	.76584			126.474	935.540
.9318	.76637	.757857		126.482	935.279
.9616	.73128			126.834	931.850
.9750	.71333	.70518	.69797	127.182	930.207
.9774	.71061	.70265	.69575	127.260	928.908
.9794	.70858	.70014	.69287	127.328	929.658
1.0	.67134	.66287	.65453	128.26	

TABLE 3

Values of the Coefficients a_i for the Equation for Excess Volume and the RMS

Mixture	a_1	a_2	a_3	a_4	RMS
Soy/acetone	-0.63964	0.56673	-0.76705	-2.95156	0.0948
Soy/n-hexane	-5.33633	-1.79139	-11.07329	-3.77605	0.268

different from the sum of the volumes of the two pure components before mixing. Usually there is a contraction in volume on mixing.

The equation

$$V^E = X_1X_2 \sum_{i=o}^{3} a_i (X_1 - X_2)$$

was fitted to express the dependence of excess volume on composition.

The values of a_i are listed in Table 3 for the two mixtures with an estimate of the RMS error.

The RMS was calculated as:

$$\mathrm{RMS} = \left[\frac{(V^E_{\mathrm{calc}} - V^E_{\mathrm{measured}})^2}{N}\right]^{1/2}$$

where N is the number of readings.

$$\tilde{V}_1 = V_1 + \frac{V^E}{X_1} + X_1X_2 \left[\frac{\delta\left(\frac{V^E}{X_1}\right)}{\delta X_1}\right]_{T,P}$$

$$\tilde{V}_2 = V_2 + \frac{V^E}{X_2} + X_1X_2 \left[\frac{\delta\left(\frac{V^E}{X_2}\right)}{\delta X_2}\right]_{T,P}$$

The results of these calculations are shown in Tables 1 and 2. Partial molar volumes are the apparent pure component molar volumes of the mixture assuming that it is ideal, i.e.:

$$V_e = X_1\tilde{V}_1 + X_2\tilde{V}_2$$

where $\tilde{V}_1$ and $\tilde{V}_2$ are the partial molar volumes at concentrations X_1 and X_2 for components 1 and 2, respectively.

These showed only a small variation from the molar volumes of the pure components. Again, this indicates that, on a molar volume basis, the two pure components are contributing to the mixture without a volume change on mixing, i.e., as an ideal mixture. This is emphasized by comparison with the large change due to volume contraction for mixtures when expressed as density, as shown in Figure 2.

For a mixture made up of large and small diameter spherical molecules it is assumed some of the small molecules pack in the interstitial spaces of the large molecules on mixing causing a reduction in volume and hence an increase in density. Apparently for the oil solvent mixtures considered here this is not so; a possible explanation is that the oil molecules are 'stringlike,' and that the solvent molecules are packing along the sides oil molecule without the interstitial spaces associated with spherical molecules.

We conclude that if the molar densities, hence, molar volumes of the pure components (oil and solvent) are known, then a straight line between these to a base of molar composition will permit the estimation of mixture molar volume from which the mixture density can be found.

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[Received May 1, 1987;
accepted November 6, 1987]