

Figure 3. Acetone-methanol system saturated with  $\text{CH}_3\text{COOK}$  and  $\text{NaBr}$

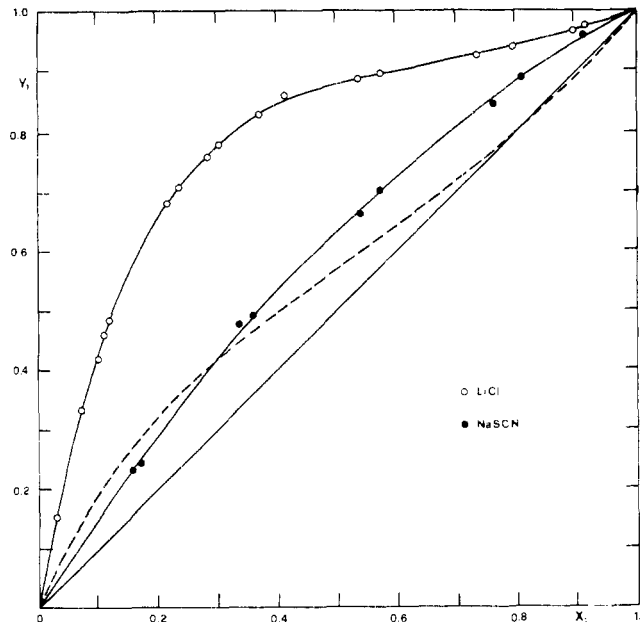


Figure 4. Acetone-methanol system saturated with  $\text{LiCl}$  and  $\text{NaSCN}$

The crossover effect, verified by Proszk and Kollar, appears at saturation only in the case of  $\text{NaI}$  and does not appear in the case of  $\text{LiCl}$  which has a very large solubility at saturation in pure methanol.

Besides the practical utility of the reported experimental data, it is to be hoped that the various patterns of behavior of these systems could provide information needed for a breakthrough in understanding the salt solutions.

#### Acknowledgment

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## Densities of Benzene-*n*-Alkane Mixtures

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Densities of mixtures of benzene with four *n*-alkanes  $\text{C}_6$ ,  $\text{C}_7$ ,  $\text{C}_{10}$ , and  $\text{C}_{16}$  were determined at 25 and 50 °C using a pycnometric method. The density measurements were used to extend the corresponding states method of Rowlinson and coworkers to systems containing benzene and long-chain hydrocarbons.

Densities of mixtures are required in chemical engineering design calculations. They are also of importance in the theoretical investigation of excess thermodynamic properties of mixtures. Recently, Mollerup and Rowlinson (4) have shown that the corresponding states method of Rowlinson and Watson (6) may be used to predict densities of liquefied natural

gases and of lower molecular weight hydrocarbons. The method is extended here to mixtures containing benzene and the higher molecular weight *n*-alkanes. Experimental data for the mixtures investigated are limited [Nigam et al. (5), Yuan et al. (8)]; therefore, an experimental study was also undertaken.

#### Experimental Method

Density measurements were made using 1- and 5-ml pycnometers. The side arms were 80 mm long with 0.7-mm diameter bore in both pycnometers. Measurements of volume were made with the pycnometers held in a constant temperature tank in which a NPL calibrated mercury in glass thermometer having 0.1 °C increments was used to measure the bath temperature. The temperature in the bath was kept constant to  $\pm 0.1$  °C.

Solutions were made using research grade pure components whose measured densities agreed with literature values (Table I). Calibration of the pycnometers was carried out using double distilled water.

The reproducibility and uncertainty of the densities were  $\pm 0.1\%$  for the 1-ml pycnometer and  $\pm 0.02\%$  for the 5-ml pycnometer.

### Prediction Method

Densities were also predicted using the corresponding states method. Briefly, the method states that the pressure of a mixture at a given temperature ( $T$ ), density ( $\rho$ ), and composition ( $\mathbf{x}$ ) may be obtained from the pressure of a reference substance  $o$  at temperature  $T/f$  and density  $\rho h$  using:

$$P[\rho, T, \mathbf{x}] = (f/h)P_o[\rho h, T/f] \quad (1)$$

Here,  $f$  and  $h$  are corresponding states parameters which depend on the composition of the mixture via the van der Waals one-fluid approximation:

$$h = \sum_i \sum_j x_i x_j h_{ij} \quad (2)$$

and

$$fh = \sum_i \sum_j x_i x_j h_{ij} f_{ij} \quad (3)$$

The pure component parameters  $h_{ii}$  and  $f_{ii}$  may be obtained from the critical constants using

$$f_{ii} = (T_{ii}^c/T_o^c) \cdot \theta_{ii,o} \quad (4)$$

and

$$h_{ii} = (V_{ii}^c/V_o^c) \cdot \Phi_{ii,o} \quad (5)$$

where  $\theta_{ii,o}$  and  $\Phi_{ii,o}$  are "shape factors" of component  $i$  relative to the reference substance  $o$ . Shape factors for the  $n$ -alkanes (up to  $C_{12}$ ) relative to methane have been evaluated by Leach et al. (3) and are given by:

$$\theta_{ii,o} = 1 + (\omega_{ii} - \omega_o)\{0.0892 - 0.8493 \ln T_{R_i} + (0.3063 - 0.4506/T_{R_i})(V_{R_i} - 0.5)\} \quad (6)$$

$$\Phi_{ii,o} = (Z_o^c/Z_{ii}^c)\{1 + (\omega_{ii} - \omega_o)[0.3903(V_{R_i} - 1.0177) - 0.9426(V_{R_i} - 0.7663) \ln T_{R_i}]\} \quad (7)$$

The  $\omega$ 's are acentric factors, and the reduced temperature and reduced volume are given by:

$$V_{R_i} = (\Phi_{ii,o}/\rho V_o^c h) \quad (8)$$

$$T_{R_i} = (T\theta_{ii,o}/T_o^c f) \quad (9)$$

When  $V_{R_i} > 2$ , the value of  $V_{R_i}$  in both Equations 6 and 7 is set equal to 2.0. When  $V_{R_i} < 0.5$ , it is set equal to 0.5. Similarly, when  $T_{R_i} > 2.0$ , the value of  $T_{R_i}$  in both equations is set equal to 2.0. Thus, the shape factors are slowly varying functions of temperature, density, and composition in a mixture. Shape factor equations for the  $n$ -alkanes have been successfully used for other simple molecules such as Ar,  $CO_2$ , CO,  $CH_4$ ,  $O_2$ , and  $N_2$  [Teja and Rowlinson (7)].

The cross parameters  $f_{ij}$  and  $h_{ij}$  may be obtained from the mixing rules

$$f_{ij} = \xi_{ij}(f_{ii}f_{jj})^{1/2} \quad (10)$$

and

$$h_{ij} = \eta_{ij} \left\{ \frac{1}{2} (h_{ii}^{1/3} + h_{jj}^{1/3}) \right\}^3 \quad (11)$$

where  $\xi_{ij}$  and  $\eta_{ij}$  are constants which must be obtained from binary data. In the absence of such data  $\xi_{ij} = 1.0$  and  $\eta_{ij} = 1.0$ .

**Table I. Comparison of Measured Pure Component Densities at 25 °C with Literature Values**

Substance	Exptl density, kg mol <sup>-3</sup>	Lit value, API Project 44
Benzene	11.190 ± 2	11.186
Hexane	7.605 ± 2	7.598
Heptane	6.783 ± 7	6.781
Decane	5.112 ± 5	5.104
Hexadecane	3.410 ± 1	3.400

**Table II. Experimental and Predicted Densities of Benzene- $n$ -Hexane Mixtures**

Predictions made with no adjustable parameters, i.e., with  $\xi_{12} = 1.0$  and  $\eta_{12} = 1.0$ . Densities in k-mol m<sup>-3</sup>

Mole fraction benzene, $x$	Density at 25 °C		Density at 50 °C	
	Exptl	Predicted	Exptl	Predicted
1.000	11.190 ± 2	11.0054	10.834 ± 2	10.6605
0.8973	10.661 ± 2	10.5458	10.325 ± 2	10.2073
0.8136	10.256 ± 2	10.1935	9.929 ± 2	9.8600
0.6652	9.555 ± 2	9.6132	9.250 ± 2	9.2844
0.5709	9.261 ± 2	9.2711	8.957 ± 2	8.9517
0.5284	9.115 ± 2	9.1232	8.810 ± 2	8.8062
0.3722	8.597 ± 2	8.6104	8.307 ± 2	8.3019
0.3163	8.432 ± 2	8.4378	8.134 ± 2	8.1322
0.2158	8.147 ± 2	8.1408	7.867 ± 2	7.8405
0.1026	7.859 ± 2	7.8255	7.589 ± 2	7.5308
0.0000	7.605 ± 2	7.5559	7.335 ± 2	7.2662

**Table III. Experimental and Predicted Densities of Benzene- $n$ -Heptane Mixtures**

Predictions made with  $\xi_{12} = 0.99$ ,  $\eta_{12} = 1.0$

Mole fraction benzene, $x$	Density at 25 °C		Density at 50 °C	
	Exptl	Predicted	Exptl	Predicted
1.0000	11.190 ± 2	11.0054	10.834 ± 2	10.6605
0.9026	10.493 ± 10	10.4263	10.165 ± 10	10.0931
0.7974	9.843 ± 10	9.8189	9.534 ± 10	9.4987
0.6973	9.302 ± 2	9.3129	9.014 ± 2	9.0041
0.5968	8.815 ± 9	8.8492	8.543 ± 9	8.5515
0.4987	8.395 ± 8	8.4343	8.132 ± 8	8.1468
0.4041	8.032 ± 8	8.0653	7.782 ± 8	7.7873
0.3019	7.661 ± 2	7.6973	7.428 ± 2	7.4290
0.2107	7.384 ± 7	7.3928	7.150 ± 7	7.1329
0.1064	7.075 ± 2	7.0694	6.849 ± 2	6.8186
0.0000	6.783 ± 7	6.764	6.567 ± 7	6.5219

**Table IV. Experimental and Predicted Densities of Benzene- $n$ -Decane Mixtures**

Predictions made with  $\xi_{12} = 0.89$  and  $\eta_{12} = 1.0$

Mole fraction benzene, $x$	Densities at 25 °C		Densities at 50 °C	
	Exptl	Predicted	Exptl	Predicted
1.0000	11.190 ± 2	11.0054	10.834 ± 2	10.6605
0.9018	9.983 ± 10	9.8790	9.680 ± 10	9.5549
0.7944	8.931 ± 2	8.8916	8.668 ± 2	8.5913
0.7012	8.210 ± 8	8.1881	7.972 ± 8	7.9081
0.6074	7.579 ± 8	7.5888	7.367 ± 7	7.3282
0.5022	6.982 ± 2	7.0116	6.788 ± 2	6.7763
0.4014	6.507 ± 7	6.5362	6.332 ± 6	6.3232
0.2923	6.054 ± 6	6.0921	5.891 ± 6	5.8978
0.1959	5.709 ± 6	5.7485	5.516 ± 6	5.5653
0.1001	5.401 ± 2	5.4357	5.227 ± 2	5.2703
0.0000	5.112 ± 5	5.1201	4.976 ± 5	4.9943

**Table V. Experimental and Predicted Densities of Benzene-*n*-Hexadecane Mixtures**  
Predictions made with  $\xi_{12} = 0.70$  and  $\eta_{12} = 1.0$

Mole fraction benzene, $x$	Densities at 25 °C		Densities at 50 °C	
	Exptl	Predicted	Exptl	Predicted
1.0000	11.190 ± 2	11.0054	10.834 ± 2	10.6605
0.9078	9.189 ± 9	9.0523	8.931 ± 9	8.7273
0.8018	7.639 ± 2	7.5683	7.400 ± 2	7.2785
0.7149	6.719 ± 7	6.7139	6.544 ± 7	6.4540
0.6117	5.887 ± 6	5.9458	5.738 ± 6	5.7254
0.4962	5.175 ± 5	5.2856	5.047 ± 5	5.1059
0.4004	4.699 ± 5	4.8495	4.586 ± 5	4.6875
0.3057	4.309 ± 1	4.4754	4.212 ± 1	4.3409
0.2035	3.966 ± 4	4.0738	3.871 ± 4	4.0203
0.0000	3.410 ± 1	3.4134	3.330 ± 1	3.3939

**Table VI. Physical Constants Required in Calculations**

Substance	$T_c$ , K	$P_c$ , bar	$V_c$ , m <sup>3</sup> kg mol <sup>-1</sup>	$Z_c$	$\omega$
Methane (ref)	190.77	46.27	0.0990	0.2889	0.0109
Benzene	562.2	49.20	0.2535	0.2668	0.2110
<i>n</i> -Hexane	508.0	30.30	0.3680	0.2640	0.3033
<i>n</i> -Heptane	540.4	27.40	0.4260	0.2598	0.3499
<i>n</i> -Decane	619.0	21.10	0.6020	0.2468	0.4801
<i>n</i> -Hexadecane	717.0	14.18	0.9500	0.2260	0.7040

**Table VII. Summary of Average and Maximum Errors for Benzene-*n*-Alkane Systems**

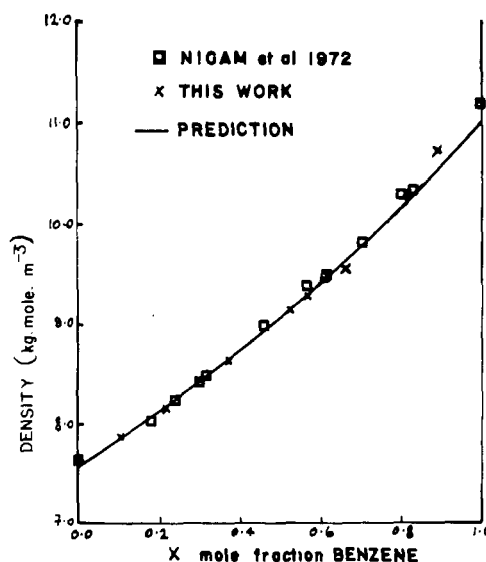
Average absolute error defined as  $(|\rho_{\text{calc}} - \rho_{\text{expt}}| / \rho_{\text{expt}}) \times 100$

System	Temp, °C	Average absolute error, %	Max error, %
Benzene- <i>n</i> -hexane	25	0.50	1.65 <sup>a</sup>
	50	0.55	1.60 <sup>a</sup>
Benzene- <i>n</i> -heptane	25	0.44	1.65 <sup>a</sup>
	50	0.41	1.60 <sup>a</sup>
Benzene- <i>n</i> -decane	25	0.59	1.65 <sup>a</sup>
	50	0.71	1.60 <sup>a</sup>
Benzene- <i>n</i> -hexadecane	25	1.72	-3.86
	50	1.93	-3.86

<sup>a</sup> Maximum error occurs for pure benzene.

## Results and Discussion

Experimental and predicted results are tabulated in Tables II-V, using physical constants of pure substances shown in Table VI. In the prediction, methane was used as a reference substance as an accurate analytical equation of state—that of Bender (2) was available for this substance. The shape factor equations (Equations 6 and 7) of Leach et al. were used for benzene, although these have been correlated for the *n*-alkanes only. As can be seen from the tables, the maximum error in the predicted density of pure benzene was only 1.65%. The errors between prediction and experiment are summarized in Table VII. Agreement between prediction and experiment is very good except for benzene-*n*-hexadecane mixtures. This is not surprising since the properties of both the pure substances deviate markedly from the properties of pure methane; hence, the results calculated using what is essentially a first-order perturbation treatment are not as accurate for these mixtures as for mixtures containing smaller



**Figure 1.** Comparison of predicted and measured densities for benzene-*n*-hexane at 25 °C

molecules. Nevertheless, an average absolute deviation of 0.65% for benzene-*n*-decane and of 1.82% for benzene-*n*-hexadecane mixtures is satisfactory. The values of  $\xi_{12}$  for each mixture were obtained by minimizing the average absolute deviation in the densities. Experimental [this work and Nigam et al. (5)] and predicted results for benzene-*n*-hexane mixtures are shown in Figure 1.

## Nomenclature

$f$  = corresponding states energy parameter  
 $h$  = corresponding states volume parameter  
 $P$  = pressure, bar  
 $R$  = gas constant, bar m<sup>3</sup> kg mol<sup>-1</sup> K<sup>-1</sup>  
 $T$  = thermodynamic temperature, K  
 $V$  = molar volume, m<sup>3</sup> kg mol<sup>-1</sup>  
 $x$  = mole fraction  
 $\mathbf{x}$  = composition vector  $x_1, x_2, \dots, x_n$   
 $Z$  = compressibility  
 $\theta, \Phi$  = shape factors  
 $\xi, \eta$  = binary interaction constants  
 $\rho$  = density, kg mol m<sup>-3</sup>  
 $\omega$  = Pitzer's acentric factor

## Subscripts

calc = calculated value  
expt = experimental value  
 $i, j$  = general components  
 $o$  = reference substance  
 $R$  = reduced state

## Superscript

$c$  = critical state

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