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LIQUID PHASE *PVT* DATA FOR BINARY MIXTURES OF TOLUENE WITH NITROETHANE AND ACETONE, AND BENZENE WITH ACETONITRILE, NITROMETHANE, AND ETHANOL

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ABSTRACT

Liquid phase *PVT* data were obtained at 0°C, 45°C, and 90°C for pressures up to 217.7 atm for various binary mixtures of toluene–nitroethane, toluene–acetone, acetonitrile–benzene, nitromethane–benzene, and ethanol–benzene. Such data are required for purposes of converting excess thermodynamic property data from a constant pressure basis to a constant volume basis. Data are presented for each pure component and for three separate mole fractions for each binary pair. Because benzene solidifies at 5.5°C, data for pure benzene are reported at 12°C rather than 0°C.

INTRODUCTION

If one desires to compute experimental values of excess thermodynamic functions on a constant volume basis for comparison with certain theoretical models, one requires data on the liquid phase compressibility and *PVT* relations of the solutions. Data on excess volumes of the solutions are also required for the conversion calculations. In a study conducted in the Thermochemical Institute laboratories it was necessary to perform such calculations for a number of binary solutions. A search of the literature revealed a complete absence of the desired *PVT* and excess volume data for the binary pairs of interest. Therefore, the necessary experimental apparatus was assembled or constructed to enable us to measure the desired quantities for the binary systems of interest. This paper contains a description of the apparatus used, the experiments performed, and the results obtained for mixtures of the five binary systems.

APPARATUS

Liquid phase *PVT* data, from which compressibilities may be calculated, were

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* Now with Amalgamated Sugar Co., Ogden, Utah, U.S.A.

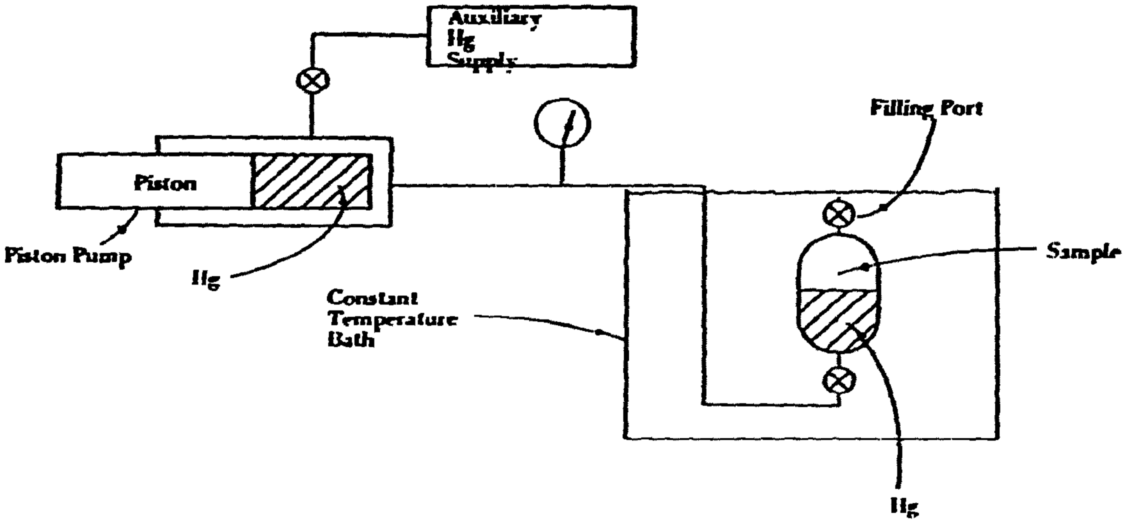

Fig. 1. Schematic diagram of liquid phase *PVT* apparatus.

measured directly. Gas chromatography was used to detect any impurity present in the samples. Chromatograms obtained therefrom showed that chemicals used had a purity quotient of 99.9 and above. The apparatus used is illustrated schematically in Fig. 1. A carefully weighed, degassed sample of liquid solution of known composition[1] was placed in a stainless steel pressure cylinder of known volume. The weight of a given sample was determined by a precision electronic balance capable of ± 0.0001 g precision. Masses of samples charged to the cell in the present experiments ranged from 71.7500 to 133.8080 g. The relatively large sample sizes were used in order to obtain better precision in the values of the liquid specific volumes.

The sample cylinder was connected by means of high pressure stainless steel tubing to the outlet port of a Ruska Model 2200 hand-driven positive displacement pump. The working fluid in the pump and lines was mercury. An auxiliary mercury supply was attached to the intake port of the pump to permit filling or emptying of the pump cylinder. Pressures were measured directly from the pump manifold by means of a Heise pressure gauge having a range of 0–340 atm (0–5000 psi) with a minimum resolution precision of ± 0.34 atm (± 5 psi).

The test cell was immersed at all times in a constant temperature bath. Three separate bath fluids (ice–water, water, polyglycol) were used to obtain bath temperatures of 0, 45, and 90°C, respectively. These temperatures were controlled by means of electronic controlling devices to ± 0.01 °C. The data for pure benzene were obtained at 12°C since benzene solidifies at 5.5°C.

The pump used is a hand-operated positive displacement piston/cylinder affair driven by a precision measuring screw. It was calibrated by calibrating the screw movement thus permitting volumes to be measured to a precision of ± 0.01 cm^3. Temperatures were measured with calibrated Beckman thermometers.

EXPERIMENTAL PROCEDURE

The pump cylinder and manifold connecting lines were filled with mercury and bled of air. In order to avoid trapping air in the system mercury was repeatedly charged and flushed through the pump cylinder and manifold assembly. The entire pump cylinder and manifold system were then pressurized to test for the presence or absence of air pockets. These latter could be detected by a gradually falling pressure reading. A steady pressure gauge reading indicated an air-free system had been achieved.

Using a dried, long-tipped hypodermic syringe, a liquid sample was drawn from beneath the surface of a previously prepared liquid mixture contained in a sample bottle, and the filled syringe was weighed. The sample was then slowly transferred into the test cylinder by inserting the syringe needle through the filling port. The liquid sample was carefully poured into the cell at the surface of the liquid to minimize flashing of the sample. After the sample was charged, the syringe was again weighed and the sample weight determined by difference.

Since contact of the sample with air could not be avoided, a small loss of some of the sample inevitably occurred. The amount of the components lost was assumed to be equal to the amount needed to saturate the air space above the liquid level. Introduction of mercury at the bottom of the cell resulted in displacement of an equal volume of air, saturated with the sample. Assuming an ideal vapor mixture, corrections were applied to the sample weight to account for this evaporation loss. For each filling of the cylinder the liquid level was brought to a predetermined mark and the plug was seated a fixed number of turns to a predetermined calibration mark. From the measured volume of the mercury forced into the cell by the pump and the calibrated cell volume, the initial volume of the liquid sample could be determined. For consistency of reference all initial measurements were made at 27.2 atm, this being a convenient and reproducible point.

After the cell had been placed in the constant temperature bath and equilibrated, a series of measurements of pressure and volume were made. The pump was turned to inject mercury into the test cell so as to cause 27 atm pressure increments. After each addition of mercury to the cell, sufficient time was allowed for full thermal equilibration. Pressure and pump scale readings were recorded and the cycle repeated. In this fashion data were obtained over the range 27–218 atm at all three temperatures 0, 45, and 90°C for samples at each liquid composition. In order to check the reproducibility of the experimental data, repeats of pump scale readings were obtained by random variation of the cell pressure. In all cases the volume readings obtained from the calibrated pump scale were reproduced within $\pm$ 0.01 cm^3. Since the pump and external manifold system were not thermostated, the ambient temperature was monitored and changes therein were used in the data reduction computer program to account for changes in pump, manifold, and cell dilations and mercury compressibility[1]. This program was used to reduce the raw data to the *PVT* data herein recorded.

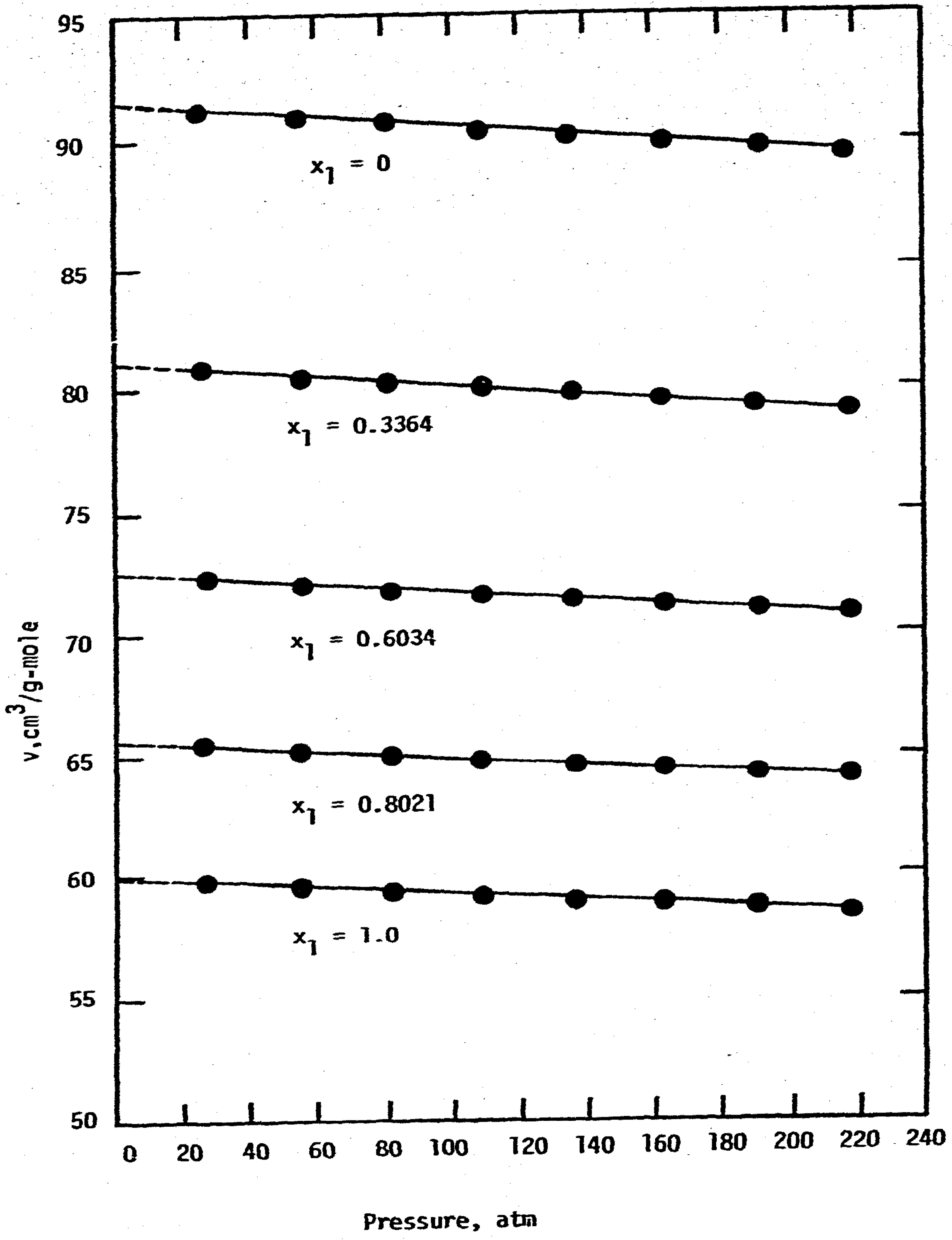

Fig. 2. Pressure-specific volume data as a function of composition for various binary mixtures of ethanol (1) – benzene (2) at 45°C.

TABLE 1

DENSITIES OF PURE COMPONENT LIQUIDS AT 45°C AND ATMOSPHERIC PRESSURE (g cm^{-3})

Component	*PVT data*	*Pycnometric data*	*Literature*	*Ref.*
Acetone	0.7636	0.7622	0.7609	2
			0.7616	3
Acetonitrile	0.7560	0.7553	0.7553	2
			0.7558	3
Benzene	0.8522	0.8522	0.8522	2
Ethanol	0.7681	0.7681	0.7684	3
Nitroethane	1.0190	1.0201	1.0169	4
Nitromethane	1.1190	1.0977	1.0977	4
			1.1033	2
Toluene	0.8410	0.8436	0.8436	3

TABLE 2

PVT DATA FOR TOLUENE (1) – NITROETHANE (2)

Pressure		*Liquid molar volumes (cm^3 gmol^{-1})*				
atm	*psi*	x_1				
		0	*0.1831*	*0.4021*	*0.6686*	*1.0*
T = 0°C						
27.22	400	70.003	76.227	83.623	92.385	104.230
54.43	800	69.892	76.028	83.435	92.187	104.045
81.65	1200	69.784	75.875	83.279	91.999	103.846
108.87	1600	69.677	75.671	83.132	91.834	103.640
136.10	2000	69.568	75.472	82.992	91.666	103.451
163.31	2400	69.460	75.269	82.855	91.491	103.267
190.53	2800	69.350	75.060	82.700	91.276	103.078
217.75	3200	69.244	74.836	82.523	91.021	102.864
T = 45°C						
27.22	400	73.491	80.165	87.845	97.017	109.270
54.43	800	73.302	79.975	87.601	96.712	108.964
81.65	1200	73.141	79.741	87.390	96.496	108.635
108.87	1600	72.960	79.555	87.176	96.218	108.387
136.10	2000	72.803	79.372	86.973	95.987	108.143
163.31	2400	72.634	79.191	86.772	95.763	107.957
190.53	2800	72.459	79.008	86.572	95.521	107.681
217.75	3200	72.285	78.836	86.358	95.299	107.397
T = 90°C						
27.22	400	77.652	84.617	92.471	102.107	114.970
54.43	800	77.392	84.328	92.169	101.741	114.518
81.65	1200	77.145	84.035	91.844	101.401	114.101
108.87	1600	76.885	83.765	91.534	101.073	113.647
136.10	2000	76.624	83.493	91.239	100.745	113.283
163.31	2400	76.362	83.233	90.948	100.431	112.899
190.53	2800	76.125	82.985	90.675	100.124	112.658
217.75	3200	75.873	82.727	90.398	99.820	112.272

RESULTS

The binary pairs studied were: toluene (1)–nitroethane (2), toluene (1)–acetone (2), acetonitrile (1)–benzene (2), nitromethane (1)–benzene (2), and ethanol (1)–benzene (2).

Table 1 contains density data for the pure component liquid calculated from the *PVT* measurements at 45°C in comparison with values measured pycnometrically at the same temperature. Both of these values are compared with literature data as cited. The agreement between the densities obtained by the present method and the other methods is considered to be acceptable.

Since the measured sample weights are precise to ± 0.0001 g, and the volumetric readings are reproducible to ± 0.01 cm^3, the specific volumes calculated therefrom on a mass basis are reported to a precision of ± 0.001 cm^3 g^{-1}. Multiplication by the

TABLE 3

PVT DATA FOR TOLUENE (1) – ACETONE (2)

Pressure		*Liquid molar volumes (cm^3 gmol^{-1})*				
atm	*psi*	x_1				
		0	*0.1874*	*0.4087*	*0.6750*	*1.0*
T = 0°C						
27.22	400	71.012	77.305	84.588	93.122	104.230
54.43	800	70.794	77.089	84.387	92.905	104.045
81.65	1200	70.607	76.892	84.181	92.706	103.846
108.87	1600	70.426	76.703	83.987	92.499	103.640
136.10	2000	70.244	76.521	83.798	92.316	103.451
163.31	2400	70.059	76.337	83.615	92.124	103.267
190.53	2800	69.887	76.152	83.429	91.927	103.078
217.75	3200	69.708	75.972	83.243	91.727	102.864
T = 45°C						
27.22	400	75.717	82.016	89.460	98.182	109.270
54.43	800	75.397	81.700	89.149	97.856	108.964
81.65	1200	75.084	81.395	88.836	97.548	108.635
108.87	1600	74.809	81.118	88.537	97.268	108.387
136.10	2000	74.525	80.851	88.268	96.985	108.143
163.31	2400	74.249	80.578	88.000	96.698	107.957
190.53	2800	73.984	80.303	87.740	96.436	107.681
217.75	3200	73.722	80.046	87.479	96.171	107.397
T = 90°C						
27.22	400	81.468	87.748	95.146	103.932	114.970
54.43	800	80.985	87.282	94.707	103.486	114.518
81.65	1200	80.513	86.834	94.265	103.045	114.101
108.87	1600	80.058	86.412	93.825	102.623	113.647
136.10	2000	79.620	86.006	93.413	102.226	113.283
163.31	2400	79.194	85.585	93.018	101.825	112.899
190.53	2800	78.803	85.197	92.631	101.440	112.658
217.75	3200	78.414	84.801	92.257	101.066	112.272

TABLE 4

PVT DATA FOR ACETONITRILE (1) – BENZENE (2)

Pressure		*Liquid molar volumes (cm^3 gmol^{-1})*				
atm	*psi*	x_1				
		0	*0.3641*	*0.6322*	*0.8373*	*1.0*
*T = 0°C**						
27.22	400	87.538	73.628	64.015	56.545	50.943
54.43	800	87.389	73.454	63.858	56.400	50.803
81.65	1200	87.223	73.290	63.712	56.261	50.675
108.87	1600	87.068	73.141	63.574	56.130	50.553
136.10	2000	86.908	72.989	63.432	56.005	50.438
163.31	2400	86.741	72.840	63.295	55.881	50.317
190.53	2800	86.582	72.693	63.153	55.755	50.207
217.75	3200	86.439	72.540	63.011	55.627	50.087
T = 45°C						
27.22	400	91.429	77.797	67.727	60.013	54.118
54.43	800	91.099	77.530	67.490	59.790	53.906
81.65	1200	90.815	77.288	67.274	59.581	53.713
108.87	1600	90.562	77.064	67.066	59.394	53.540
136.10	2000	90.303	76.856	66.872	59.218	53.377
163.31	2400	90.051	76.631	66.673	59.034	53.224
190.53	2800	89.814	76.418	66.481	58.856	53.055
217.75	3200	89.566	76.205	66.289	58.676	52.875
T = 90°C						
27.22	400	96.910	82.628	72.082	64.099	57.904
54.43	800	96.499	82.277	71.755	63.801	57.645
81.65	1200	96.097	81.928	71.436	63.506	57.367
108.87	1600	95.714	81.590	71.129	63.221	57.106
136.10	2000	95.345	81.259	70.830	62.947	56.853
163.31	2400	94.985	80.947	70.545	62.679	56.603
190.53	2800	94.643	80.638	70.275	62.408	56.372
217.75	3200	94.301	80.329	70.002	62.150	56.123

* T = 12.0°C for pure benzene for $x_1 = 0$.

known molecular weights then produces molar specific volumes precise to ± 0.001 cm^3 gmol^{-1}.

Figure 2 is a plot of the liquid phase *PVT* data obtained for the ethanol (1)–benzene (2) binary pair at 45°C. These curves are typical of those obtained for all the mixtures studied and are shown only for illustrative purposes.

Tables 2 through 6 contain the *PVT* data for the five binary systems studied. All pressures are expressed in both atm and psia (the latter being the actual units used by the manufacturer of the gauge). All compositions (x) are in mole fractions of the first component. All temperatures are given in °C, and all volumes are given in cm^3 gmol^{-1} units.

The experimental *PVT* data were fitted to a volume explicit quadratic function of pressure, $V = a + bP + cP^2$, where the parameters a, b and c were assumed to be

TABLE 5

PVT DATA FOR NITROMETHANE (1) – BENZENE (2)

Pressure		*Liquid molar volumes (cm³ gmol⁻¹)*				
atm	*psi*	x_1				
		0	*0.3557*	*0.6236*	*0.8325*	*1.0*
$T = 0°C^*$						
27.22	400	87.538	74.519	66.294	60.338	51.444
54.43	800	87.389	74.404	66.150	60.231	51.351
81.65	1200	87.223	74.244	66.020	60.123	51.265
108.87	1600	87.068	74.096	65.903	60.020	51.182
136.10	2000	86.908	73.958	65.788	59.926	51.108
163.31	2400	86.741	73.817	65.666	59.825	51.038
190.53	2800	86.582	73.686	65.558	59.722	50.946
217.75	3200	86.439	73.536	65.440	59.620	50.857
$T = 45°C$						
27.22	400	91.429	78.589	69.147	63.510	54.420
54.43	800	91.099	78.401	68.934	63.379	54.267
81.65	1200	90.815	78.179	68.748	63.230	54.132
108.87	1600	90.562	77.963	68.575	63.084	54.008
136.10	2000	90.303	77.761	68.405	62.944	53.872
163.31	2400	90.051	77.565	68.241	62.808	53.732
190.53	2800	89.814	77.359	68.080	62.673	53.589
217.75	3200	89.566	77.146	67.921	62.530	53.441
$T = 90°C$						
27.22	400	96.910	83.527	73.255	67.181	57.674
54.43	800	96.499	83.176	72.971	66.967	57.481
81.65	1200	96.097	82.822	72.713	66.759	57.548
108.87	1600	95.714	82.504	72.450	66.558	57.121
136.10	2000	95.345	82.201	72.209	66.362	56.952
163.31	2400	94.985	81.906	71.972	66.164	56.792
190.53	2800	94.643	81.573	71.740	65.966	56.627
217.75	3200	94.301	81.259	71.522	65.768	56.463

* $T = 12.0°C$ for pure benzene for $x_1 = 0$.

linear functions of temperature and composition. In all the cases investigated, the data seemed to be well represented by this simple quadratic fit so that more complex expressions were not sought.

The percent relative standard deviation, σ_y, defined as

$$\sigma_y \equiv \frac{1}{N}\left[\sum_{i=1}^{N}\left(\frac{V_{\text{exp}} - V_{\text{cal}}}{V_{\text{exp}}}\right)^2\right]^{1/2} \times 100 \tag{1}$$

(where N is the number of data points and $V_{\text{exp}}, V_{\text{cal}}$ are, respectively, the experimental and calculated values of liquid molar volumes in cm³ gmol⁻¹) was computed in all cases. In the case of toluene (1)–nitroethane (2) $\sigma_y = 0.0058\%$.

In order to estimate the accuracy of the *PVT* data, values of the isothermal compressibility

TABLE 6

PVT DATA FOR ETHANOL (1) – BENZENE (2)

Pressure		*Liquid molar volumes* (*cm*^{3} *gmol*$^{-1}$)				
atm	*psi*	x_1				
		0	*0.3364*	*0.6034*	*0.8201*	*1.0*
T = *0°C**						
27.22	400	87.538	73.584	68.549	62.189	56.925
54.43	800	87.389	73.285	68.410	62.014	56.775
81.65	1200	87.223	73.013	68.253	61.856	56.629
108.87	1600	87.068	72.655	68.105	61.705	56.490
136.10	2000	86.908	72.359	67.955	61.566	56.361
163.31	2400	86.741	72.072	67.801	61.427	56.232
190.53	2800	86.582	71.693	67.646	61.292	56.115
217.75	3200	86.439	71.891	67.492	61.152	55.972
T = *45°C*						
27.22	400	91.429	80.766	72.260	65.410	59.807
54.43	800	91.099	80.493	71.989	65.173	59.576
81.65	1200	90.815	80.230	71.758	64.938	59.360
108.87	1600	90.562	79.994	71.536	64.715	59.156
136.10	2000	90.303	79.704	71.329	64.526	58.969
163.31	2400	90.051	79.438	71.124	64.342	58.784
190.53	2800	89.814	79.166	70.921	64.154	58.583
217.75	3200	89.566	78.893	70.723	63.969	58.387
T = *90°C*						
27.22	400	96.910	86.176	76.741	69.354	63.289
54.43	800	96.499	85.762	76.387	69.015	62.992
81.65	1200	96.097	85.367	76.046	68.685	62.698
108.87	1600	95.714	84.969	75.723	68.385	62.413
136.10	2000	95.345	84.659	75.417	68.098	62.140
163.31	2400	94.985	84.238	75.130	67.824	61.884
190.53	2800	94.643	83.875	74.832	67.558	61.628
217.75	3200	94.301	83.464	74.545	67.295	61.368

* $T = 12.0$°C for pure benzene for $x_1 = 0$.

TABLE 7

COMPARISON OF ISOTHERMAL COMPRESSIBILITY COEFFICIENTS FOR PURE TOLUENE AND BENZENE AT 45°C WITH LITERATURE VALUES

Substance	$10^6\ \beta_T$ (*atm*$^{-1}$)		
	This work	*Literature*	*Ref.*
Benzene	117.3 ± 2.9	116.5 ± 2.9	5
Toluene	104.8 ± 2.9	105.2 ± 2.9	6

$$\beta_t = \frac{1}{V_0}\left|\left(\frac{\partial V}{\partial p}\right)_T\right|_{p=0} \qquad (2)$$

were calculated from the data for benzene and toluene at 45°C. Values of $\Delta V/\Delta p$ were calculated from the data and divided by the extrapolated value of V_0. These values were then plotted as a function of pressure and extrapolated to zero pressure. Table 7 contains the results of these extrapolations together with the accepted literature values[5, 6]. The agreement is seen to be satisfactory.

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