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LIQUID PHASE *PVT* DATA, EXCESS VOLUME DATA, CONSTANT VOLUME EXCESS THERMODYNAMIC FUNCTIONS, AND THERMAL PRESSURES FOR TEN BINARY MIXTURES*

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ABSTRACT

Liquid phase *PVT* data were obtained at 0°C, 45°C, and 90°C for pressures from 1–217.7 atm for various binary mixtures for the systems benzene–acetone, carbontetrachloride–acetone, acetonitrile–carbontetrachloride, toluene–acetonitrile, and ethanol–toluene. Excess volume data were obtained at 45°C for the same systems as well as for mixtures of toluene–nitroethane, toluene–acetone, acetonitrile–benzene, nitromethane–benzene, and ethanol–benzene.

Constant volume thermodynamic excess functions U_V^E, H_V^E, A_V^E, G_V^E, and TS_V^E were computed for each of the ten systems and are presented. It was found that mole fraction averages of each of these excess functions agree almost exactly with experimental values. Thermal pressures were also calculated for each of the ten systems and found to agree within 1–3% with mole fraction averages.

INTRODUCTION

The ability to correlate and predict vapor–liquid equilibrium (VLE) data quickly and accurately for non-ideal binary and multicomponent mixtures is of great interest and importance in industrial design. Some theoretical models developed for this purpose are based upon the assumption of constant volume mixing processes. Most excess property functions are derived from experimental data obtained under either isothermal or isobaric conditions. Therefore, if one wishes to consider constant volume excess functions, it is necessary to convert the experimental data to this basis. In order to make such a conversion of basis, one requires additional data on liquid phase compressibility and *PVT* behavior of mixtures together with excess volume data.

As part of a continuing study of VLE predictive techniques utilizing heat of mixing data[1–3] being carried out in the Thermochemical Institute, it was necessary

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to perform a number of such conversions. A literature search revealed a complete absence of the desired liquid phase *PVT* and excess volume data for the ten binary mixtures of interest. Therefore, the necessary experimental apparatus was assembled to allow measurement of the desired quantities. This paper, and a previous paper[3], contain a description of the experimental apparatus used together with the complete results obtained for various mixtures of the ten binary systems studied.

THEORETICAL CONSIDERATIONS

Scatchard[4] has outlined procedures for converting excess property functions from a constant pressure to a constant volume basis. His results are summarized below as

$$A_V^E = G_P^E + \frac{V}{2\beta}\left(\frac{V^E}{V}\right)^2 \qquad (1)$$

$$S_V^E = S_P^E - \alpha V^E/\beta \qquad (2)$$

$$U_V^E = H_P^E - P_T V^E \qquad (3)$$

$$G_V^E = G_P^E + V^E/\beta \qquad (4)$$

where

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad (5)$$

is the coefficient of volumetric expansion,

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (6)$$

is the isothermal compressibility of the fluid, and

$$P_T = T\alpha/\beta = T\left(\frac{\partial P}{\partial T}\right)_V \qquad (7)$$

is a quantity sometimes called the "thermal pressure".

Several different types of constant volume mixing processes have been discussed by Scott[5]. The one of interest here is where X_1 moles of component 1 at an initial pressure P and volume V_1^0 are mixed with X_2 moles of component 2 at pressure P and volume V_2^0 to form 1 mole of mixture. The pressure P_M of the mixture is then adjusted so that $\Delta V^M = 0$; that is so that $V_M = X_1 V_1^0 + X_2 V_2^0$.

In order to obtain the values of α, β, and P_T required for application of eqns (1) to (4) liquid phase *PVT* data for mixtures are required. For the systems studied and described later, it was found that a simple *PVT* expression of the form

$$V = a(X_1, T) + b(X_1, T)P + c(X_1, T)P^2 \qquad (8)$$

suffices, where a, b, and c are empirical functions determined from the data. From

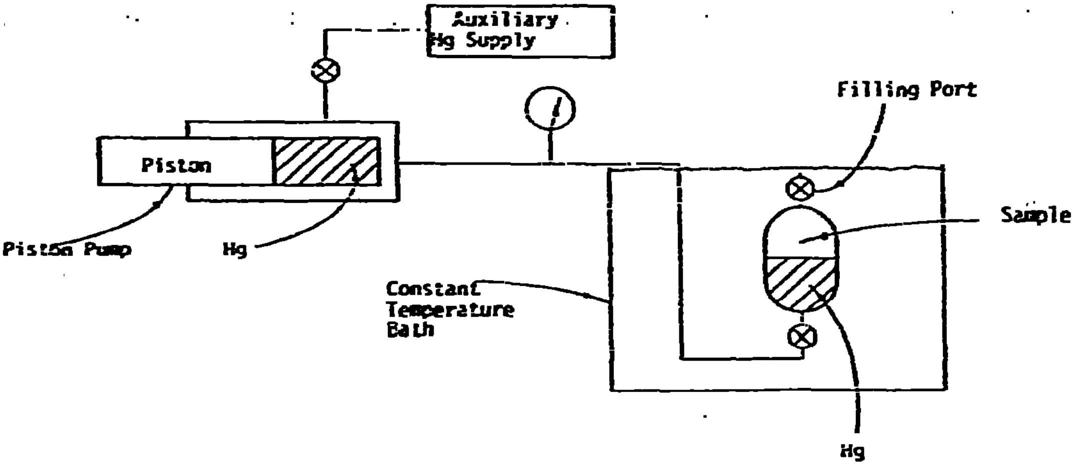

Fig. 1. Schematic flow diagram for liquid phase *PVT* apparatus.

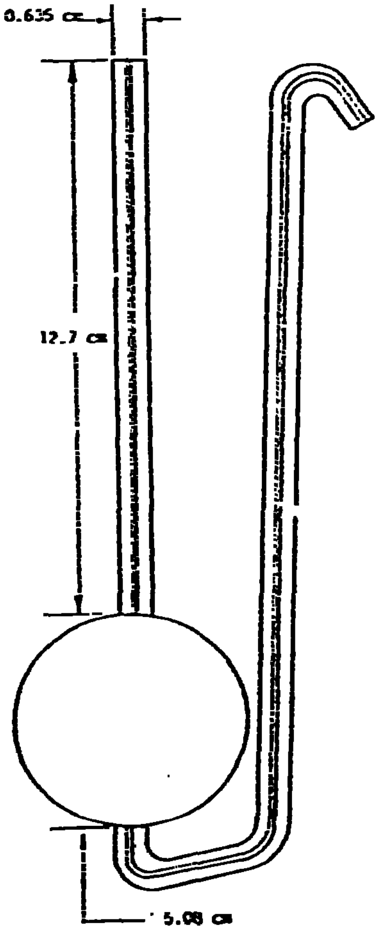

Fig. 2. Schematic diagram of pycnometers used for density measurements.

the experimental data as smoothed by eqn (8), one can compute all of the required values according to the above equations.

EXPERIMENTAL STUDY

Apparatus and procedure

The experimental apparatus and procedure used to obtain the liquid phase *PVT* data for this study have been described in detail in an earlier publication[3]. Only a brief description will be presented here. A schematic flow diagram of the apparatus is shown in Fig. 1. Carefully prepared samples were placed in the sample cylinder and then pressurized by introduction of mercury from the Ruska piston pump. The system was carefully thermostated to maintain isothermal conditions. Pressures were read from a high precision Heise gage and volumes were calculated from calibrated pump settings. Pressures were varied over the range 0–218 atm (0–3200 psi) in increments of 27 atm (400 psi) with a minimum resolution of ± 0.34 atm (± 5 psi). The test cell was maintained isothermal to ± 0.01 °C in one of three different bath fluids: ice-water (0 °C), water (45 °C) and polyglycol (90 °C).

Excess volume data were calculated from pycnometric measurements of liquid densities for samples of the solutions prepared for the *PVT* measurements. Figure 2 shows a schematic illustration of one of the pycnometers which were specially constructed for this study. Each of the capillary stems was graduated with 80 scribed markings at 0.1-cm intervals and had an internal bore diameter of 0.1 cm. The internal volume of the large bulb was approximately 50 cm^3. Precise values were determined from repeated weighings with different fillings of doubly distilled, deaerated water[6]. A calibration of volume as a function of stem-scale reading at various temperatures was obtained.

The pycnometers were initially cleaned by boiling in a cleaning solution followed by rinsing with distilled water and alcohol. Subsequent purging was accomplished by blowing dry nitrogen gas from a cylinder of compressed nitrogen through the pycnometer. A commercial Lauda temperature bath controllable to ± 0.01 °C was used for all density measurements. Temperatures were measured with a Beckman thermometer which had previously been calibrated against a NBS secondary standard thermometer. Weights were measured using a double pan chainomatic balance precise to ± 0.0001 g. The weights used were calibrated against each other for internal consistency and against an NBS standard set for absolute accuracy level.

The binary solutions used for all *PVT* and V^E measurements were prepared according to the following procedure. Once an approximate mole fraction had been decided upon, an appropriate amount of one component was carefully weighed into a mixing bottle. It was assumed that the vapor space above this liquid was saturated with the vapor phase of the substance. A carefully weighed amount of the second liquid was then introduced into the bottle by means of a long-tipped hypodermic syringe inserted below the liquid surface to create the mixture. A correction was made to the amount of the first liquid present to account for the vapor lost by displacement of saturated air–vapor mixture when the second liquid was introduced. Thereafter the bottle was sealed, shaken, and allowed to equilibrate. Corrections were also applied for evaporation of the second liquid into the vapor space. In this manner, precise mole fractions were calculated.

Samples were withdrawn using a long-tipped hypodermic syringe, placed into the carefully dried and weighed pycnometers, weighed, and immersed in a higher temperature bath for a period of time sufficient to remove bubbles of dissolved air and deaerate the samples. The filled pycnometers were then immersed in and equilibrated with the controlled temperature baths and the sample volumes determined. This was accomplished by reading the heights of the menisci in the two arms of the pycnometer, recording the average value, and obtaining the desired volume from the appropriate pycnometer calibration curve. From this volume and the measured weights, the density of the sample was calculated.

Excess specific volumes were calculated from the relation

$$V^E = (X_1M_1 + X_2M_2)/\rho_m - X_1M_1/\rho_1 - X_2M_2/\rho_2 \qquad (9)$$

where X_1, X_2 are the mole fractions of components 1 and 2, respectively, M_1, M_2 are their molecular weights, P_1, P_2 are the pure component densities, and P_m is the measured mixture density.

Experimental results

Ten binary systems were studied in this work. They are: (I) Toluene(1)-nitroethane(2); (II) toluene(1)-acetone(2); (III) acetonitrile(1)-benzene(2); (IV) nitromethane(1)-benzene(2); (V) ethanol(1)-benzene(2); (VI) benzene(1)-acetone(2); (VII) carbontetrachloride(1)-acetone(2); (VIII) acetonitrile(1)-carbontetrachloride(2); (IX) toluene(1)-acetonitrile(2); and (X) ethanol(1)-toluene(2). Experimental *PVT* data for systems I to V were presented earlier[3]. Table 1 contains liquid phase *PVT*

TABLE 1

LIQUID MOLAR VOLUMES* FOR CCl_4

Pressure		*Temperature*		
Atm	*psi*	*90°C*	*45°C*	*0°C*
27.22	400	105.033	98.991	93.870
54.43	800	104.538	98.622	93.588
81.65	1200	104.068	98.296	93.341
108.87	1600	103.605	97.983	93.125
136.10	2000	103.162	97.658	92.909
163.31	2400	102.727	97.373	92.716
190.53	2800	102.293	97.076	92.525
217.75	3200	101.876	96.786	92.288

* All volumes expressed as $cm^3\ gmol^{-1}$.

TABLE 2

LIQUID MOLAR VOLUMES[a] FOR FIVE BINARY SYSTEMS AT 0°C

Pressure		*VI*[b]			*VII*[c]		
Atm	*psi*	$X_1=0.2162$	*0.4525*	*0.7128*	*0.2029*	*0.4323*	*0.6948*
27.22	400	74.960	78.164	82.158	75.670	80.988	86.722
54.43	800	74.768	77.949	81.958	75.408	80.774	86.491
81.65	1200	74.593	77.760	81.772	75.192	80.564	86.283
108.87	1600	74.428	77.579	81.595	75.000	80.360	86.078
136.10	2000	74.271	77.405	81.417	74.821	80.165	85.891
163.31	2400	74.112	77.232	81.243	74.634	79.989	85.698
190.53	2800	73.956	77.058	81.072	74.448	79.793	85.270
217.75	3200	73.796	76.879	80.900	74.266	79.604	85.323

Pressure		*VIII*[d]			*IX*[e]		
Atm	*psi*	$X_1=0.3809$	*0.6486*	*0.8471*	*0.1398*	*0.3276*	*0.5936*
27.22	400	77.493	65.915	57.795	58.117	68.088	82.206
54.43	800	77.284	65.747	57.643	57.963	67.905	82.015
81.65	1200	77.101	65.592	57.509	57.820	67.756	81.834
108.87	1600	76.931	65.447	57.393	57.686	67.606	81.665
136.10	2000	76.757	65.303	57.273	57.558	67.468	81.501
163.31	2400	76.593	65.157	57.162	57.427	67.327	81.339
190.53	2800	76.423	65.014	57.047	57.306	67.182	81 182
217.75	3200	76.256	64.872	56.927	57.170	67.041	81.006

Pressure		*X*[f]		
Atm	*psi*	$X_1=0.3775$	*0.6451*	*0.8450*[g]
27.22	400	85.838	73.867	63.975
54.43	800	85.640	73.688	63.808
81.65	1200	85.455	73.518	63.654
108.87	1600	85.275	73.359	63.509
136.10	2000	85.099	73.202	63.366
163.31	2400	84.922	73.047	63.230
190.53	2800	84.747	72.890	63.089
217.75	3200	84.570	72.730	62.941

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[a] All volumes expressed as cm^3 gmol^{-1}.
[b] Benzene(1)–acetone(2).
[c] Carbontetrachloride(1)–acetone(2).
[d] Acetonitrile(1)–carbontetrachloride(2).
[e] Toluene(1)–acetonitrile(2).
[f] Ethanol(1)–toluene(2).
[g] Data for all pure components except CCl_4 are found in ref. 3.

TABLE 3

LIQUID MOLAR VOLUMES[a] FOR FIVE BINARY SYSTEMS AT 45 °C

Pressure		*VI*[b]			*VII*[c]		
Atm	*psi*	$X_1 = 0.2162$	*0.4525*	*0.7128*	*0.2029*	*0.4323*	*0.6948*
27.22	400	79.118	86.925	82.869	80.528	85.940	91.962
54.43	800	78.843	86.625	82.575	80.155	85.600	91.620
81.65	1200	78.575	86.342	82.279	79.828	85.293	91.279
108.87	1600	78.328	86.074	82.008	79.546	84.993	90.977
136.10	2000	78.100	85.819	81.761	79.259	84.717	90.681
163.31	2400	77.865	85.560	81.494	78.991	84.438	90.376
190.53	2800	77.631	85.312	81.246	78.723	84.179	90.072
217.75	3200	77.405	85.064	81.001	78.456	83.918	89.767

Pressure		*VIII*[d]			*IX*[e]		
Atm	*psi*	$X_1 = 0.3809$	*0.6486*	*0.8471*	*0.1398*	*0.3276*	*0.5936*
27.22	400	82.023	69.918	61.100	61.629	71.957	86.507
54.43	800	81.722	69.667	60.894	61.427	71.715	86.256
81.65	1200	81.442	69.430	60.694	61.225	71.484	85.993
108.87	1600	81.174	69.208	60.505	61.007	71.293	85.756
136.10	2000	80.925	68.987	60.341	60.820	71.064	85.514
163.31	2400	80.684	68.778	60.194	60.615	70.854	85.286
190.53	2800	80.430	68.566	60.033	60.433	70.647	85.037
217.75	3200	80.175	68.359	59.833	60.247	70.443	84.793

Pressure		*X*[f]		
Atm	*psi*	$X_1 = 0.3775$	*0.6451*	*0.8450*
27.22	400	90.275	77.384	67.221
54.43	800	90.027	77.116	66.978
81.65	1200	89.746	76.879	66.759
108.87	1600	89.496	76.654	66.555
136.10	2000	89.240	76.434	66.351
163.31	2400	88.989	76.214	66.149
190.53	2800	88.746	75.995	65.967
217.75	3200	88.495	75.780	65.774

[a] All volumes expressed as $cm^3\ gmol^{-1}$

[b] Benzene(1)–acetone(2).

[c] Carbontetrachloride(1)–acetone(2).

[d] Acetonitrile(1)–carbontetrachloride(2).

[e] Toluene(1)–acetonitrile(2).

[f] Ethanol(1)–toluene(2).

TABLE 4

LIQUID MOLAR VOLUMES[a] FOR FIVE BINARY SYSTEMS AT 90°C

Pressure		*VI*[b]			*VII*[c]		
Atm	*psi*	$X_1 = 0.2162$	0.4525	0.7128	0.2029	0.4323	0.6948
27.22	400	84.174	88.461	92.444	86.479	91.757	98.101
54.43	800	83.788	88.034	92.042	85.957	91.243	97.556
81.65	1200	83.400	87.613	91.630	85.460	90.763	97.055
108.87	1600	83.017	87.190	91.234	84.984	90.286	96.600
136.10	2000	82.649	86.799	90.861	84.543	89.849	96.153
163.31	2400	82.300	86.418	90.482	84.114	89.414	95.704
190.53	2800	81.951	86.050	90.118	83.695	88.983	95.312
217.75	3200	81.609	85.687	89.761	83.308	88.555	94.897

Pressure		*VIII*[d]			*IX*[e]		
Atm	*psi*	$X_1 = 0.3809$	0.6486	0.8471	0.1398	0.3276	0.5936
27.22	400	87.427	73.987	65.131	65.730	76.517	91.525
54.43	800	87.001	73.607	64.852	65.443	76.153	91.157
81.65	1200	86.589	73.245	64.557	65.141	75.824	90.799
108.87	1600	86.194	72.901	64.274	64.842	75.505	90.454
136.10	2000	85.807	72.563	64.014	64.576	75.211	90.160
163.31	2400	85.434	72.241	63.740	64.296	74.932	89.783
190.53	2800	85.064	71.937	63.490	64.037	74.643	89.457
217.75	3200	84.705	71.627	63.238	63.772	74.297	89.142

Pressure		*X*[f]		
Atm	*psi*	$X_1 = 0.3775$	0.6451	0.8450
27.22	400	95.560	81.975	71.163
54.43	800	95.226	81.606	70.827
81.65	1200	94.851	81.252	70.512
108.87	1600	94.476	80.916	70.219
136.10	2000	94.126	80.602	69.930
163.31	2400	93.765	80.281	69.649
190.53	2800	93.436	79.977	69.377
217.75	3200	93.085	79.642	69.109

[a] All volumes expressed as cm^3 $gmol^{-1}$.

[b] Benzene(1)–acetone(2).

[c] Carbontetrachloride(1)–acetone(2).

[d] Acetonitrile(1)–carbontetrachloride(2).

[e] Toluene(1)–acetonitrile(2).

[f] Ethanol(1)–toluene(2).

TABLE 5

EXCESS VOLUME DATA AT 45 °C FOR THE TEN BINARY SYSTEMS STUDIED

System I^{a}		II^{b}		III^{c}		IV^{d}		V^{e}	
X_1	$V^{E\,f}$	X_1	V^{E}	X_1	V^{E}	X_1	V^{E}	X_1	V^{E}
0.144	−0.063	0.147	−0.172	0.273	−0.183	0.291	0.102	0.276	0.142
0.309	−0.093	0.316	−0.280	0.530	−0.075	0.524	0.168	0.503	0.108
0.504	−0.095	0.409	−0.318	0.719	−0.024	0.713	0.172	0.692	0.026
0.671	−0.086	0.510	−0.321	0.836	+0.124	0.862	0.100	0.820	−0.035
0.764	−0.055	0.735	−0.201	0.908	0.031	0.937	0.053	0.900	−0.034

[a] Toluene(1)–nitroethane(2).

[b] Toluene(1)-acetone(2).

[c] Acetonitrile(1)–benzene(2).

[d] Nitromethane(1)–benzene(2).

[e] Ethanol(1)–benzene(2).

[f] All V^{E} are in cm^3 gmol^{-1}. Values are precise to ± 0.003 cm^3 gmol^{-1}.

System VI^{g}		VII^{h}		$VIII^{i}$		IX^{j}		$X^{k,l}$	
X_1	V^{E}	X_1	V^{E}	X_1	V^{E}	X_1	V^{E}	X_1	V^{E}
0.171	−0.062	0.160	−0.048	0.315	−0.048	0.110	−0.033	0.312	−1.22
0.355	−0.069	—	—	0.552	−0.057	0.247	−0.074	0.547	−1.12
0.556	−0.107	0.433	−0.047	—	—	0.426	−0.171	0.732	−1.07
0.768	−0.083	0.534	−0.080	0.880	−0.084	0.665	−0.239	0.880	−0.973
0.882	−0.034	0.750	−0.003	0.943	−0.007	0.816	−0.172	0.942	−0.888

[g] Benzene(1)-acetone(2).

[h] Carbontetrachloride(1)–acetone(2).

[i] Acetonitrile(1) carbontetrachloride(2).

[j] Toluene(1)-acetonitrile(2).

[k] Ethanol(1)–toluene(2).

[l] T = 35 °C for these data.

data for CCl_4. Tables 2–4 contain liquid phase *PVT* data for various mixtures of the five binary systems VI–X. Data for benzene, acetone, acetonitrile and ethanol were presented earlier[3].

Pure component liquid densities for seven of the eight substances used in the present study were presented earlier[3]. The density of CCl_4 as determined pycnometrically at 45 °C was 1.5457 ± 0.0001 g cm^{-3}. The value determined by extrapolation of the *PVT* data to atmospheric pressure was 1.548 ± 0.002 g cm^{-3}. These compare favorably with the literature values of 1.5422 g cm^{-3} and 1.5456 g cm^{-3} reported by Brown and Smith[7] and Gunter et al.[8], respectively.

Table 5 contains the excess volume data obtained for all ten systems. Figure 3 is a plot of the *PVT* data for system IX at 90 °C which illustrates typical behavior for all of the five systems VI to X at all temperatures.

From these data and eqns (1) through (8), values of various excess thermodynamic functions at constant volume were calculated. Tables 6 through 8 contain the results of these calculations. The thermodynamic functions U_V^E, H_V^E, A_V^E, G_V^E and TS_V^E are presented for each of the ten systems. The constant volume excess thermo-

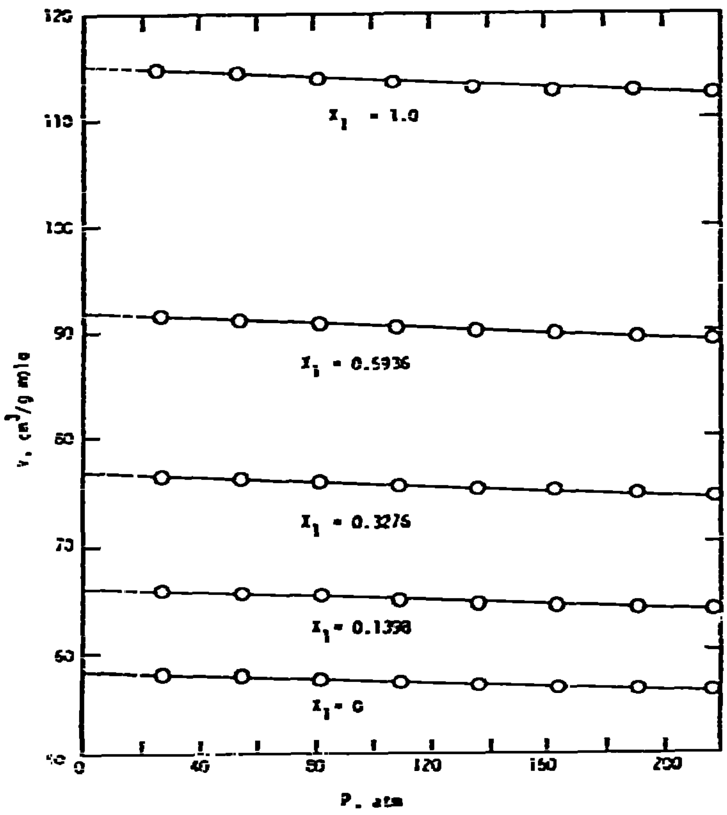

Fig. 3. Pressure-specific volume data as a function of composition for the toluene(1)–acetonitrile(2) system at 90°C.

dynamic functions are displayed graphically in Figs. 4 and 5 for systems I and X, respectively, to illustrate typical behavior of the systems studied.

The labor involved in obtaining liquid phase *PVT* data and V^E data for mixtures and then converting M_P^E to M_V^E (M_P^E, M_V^E are respectively the excess thermodynamic function M^E on constant pressure or volume basis) is considerable. It would be most desirable, if one could adequately calculate values for mixtures as mole fraction averages of the pure component values; that is, compute

$$M_V^E = X_1 M_{V1} + X_2 M_{V2} \tag{10}$$

Average values such as this were calculated for each of the energy functions tabulated in Tables 6 through 8 and almost perfect agreement was found. This is illustrated for system III in Table 9 as a typical case. Clearly, the use of $\overline{M}_V^E$ calculated according to eqn (10) is perfectly adequate in place of M_V^E measured experimentally. This represents great savings in time and labor.

Table 10 contains values of thermal pressures, P_T, as computed from the data according to eqn (7) for each of the systems. Also included are $\bar{P}_T$ values computed according to eqn (10) for comparison purposes. The agreement between P_T and $\bar{P}_T$

TABLE 6

CONSTANT VOLUME EXCESS THERMODYNAMIC FUNCTIONS[a] FOR BINARY MIXTURES I TO IV AT 45°C

X_1	I[b]					II[c]				
	U_V^E	H_V^E	A_V^E	G_V^E	TS_V^E	U_V^E	H_V^E	A_V^E	G_V^E	TS_V^E
0.1	38.06	28.12	42.49	32.54	− 4.42	28.04	11.22	38.05	21.23	−10.00
0.2	65.94	48.80	75.20	58.05	− 9.26	51.90	18.81	67.51	34.42	−15.61
0.3	84.00	63.04	98.93	77.95	−14.92	69.38	23.67	88.43	42.72	−19.05
0.4	93.12	71.00	114.06	91.95	−20.94	79.56	26.03	100.89	47.36	−21.33
0.5	94.08	72.91	120.64	99.47	−26.56	82.01	26.24	104.93	49.15	−22.92
0.6	87.58	68.99	118.32	99.72	−30.74	76.81	24.62	100.58	48.39	−23.77
0.7	74.29	59.55	106.38	91.64	−32.09	64.57	21.45	87.90	44.78	−20.34
0.8	54.77	44.91	83.72	73.85	−28.95	46.38	16.78	66.91	37.31	−23.53
0.9	29.58	25.42	48.88	44.71	−19.29	23.87	10.35	37.61	24.09	−13.74

X_1	III[d]					IV[e]				
	U_V^E	H_V^E	A_V^E	G_V^E	TS_V^E	U_V^E	H_V^E	A_V^E	G_V^E	TS_V^E
0.1	52.53	29.05	62.53	39.05	−10.00	62.75	69.96	63.69	70.90	−0.94
0.2	86.99	53.46	107.78	74.25	−20.78	110.74	126.11	114.60	129.97	−3.86
0.3	107.96	74.64	138.16	104.84	−30.20	145.37	170.02	152.21	176.86	−6.83
0.4	119.26	92.26	155.48	128.48	−36.22	167.92	201.35	176.01	209.45	−8.09
0.5	123.11	105.21	160.84	142.93	−37.72	178.67	218.93	185.50	226.41	−6.83
0.6	120.21	111.55	154.68	146.02	−34.47	176.96	220.74	180.14	224.64	−3.18
0.7	109.62	108.43	136.77	135.57	−27.14	161.19	203.96	159.42	202.89	−1.77
0.8	88.91	92.13	106.19	109.41	−17.28	128.82	164.90	122.83	159.56	+5.99
0.9	54.04	58.04	61.35	65.35	− 7.31	76.36	98.99	69.85	92.89	+6.53

[a] All functions expressed as cal gmol^{-1}.
[b] Toluene(1)–nitroethane(2).
[c] Toluene(1)–acetone(2).
[d] Acetonitrile(1)–benzene(2).
[e] Nitromethane(1)–benzene(2).

TABLE 7

CONSTANT VOLUME EXCESS THERMODYNAMIC FUNCTIONS[a] FOR BINARY MIXTURES V TO VIII AT 45°C

X_1	V^b					VI^c				
	U_V^E	H_V^E	A_V^E	G_V^E	TS_V^E	U_V^E	H_V^E	A_V^E	G_V^E	TS_V^E
0.1	196.19	211.33	121.58	136.72	74.62	14.39	10.92	22.54	19.07	−8.15
0.2	291.46	314.95	201.91	225.39	89.56	26.00	18.00	41.27	33.27	−15.27
0.3	318.83	345.48	249.05	275.70	69.78	34.83	23.03	55.73	43.93	−20.90
0.4	305.18	330.19	269.49	294.50	35.69	41.23	26.58	65.49	50.84	−24.26
0.5	270.50	290.00	268.19	287.69	2.31	45.15	28.84	70.08	53.78	−24.93
0.6	227.83	239.45	248.54	260.16	−20.71	46.16	29.63	69.07	52.53	−22.91
0.7	183.38	186.71	212.40	215.73	−29.02	43.46	28.38	62.00	46.92	−18.54
0.8	136.55	133.54	160.04	157.02	−23.49	35.84	24.14	48.43	36.73	−12.59
0.9	79.95	75.25	90.18	85.48	−10.23	21.75	15.61	27.91	21.78	−6.17

X_1	VII^d					$VIII^e$				
	U_V^E	H_V^E	A_V^E	G_V^E	TS_V^E	U_V^E	H_V^E	A_V^E	G_V^E	TS_V^E
0.1	10.65	13.81	42.81	45.97	−32.16	121.24	117.73	120.00	116.48	+1.24
0.2	22.76	23.23	76.75	77.22	−53.99	188.48	182.82	202.25	196.59	−13.77
0.3	36.23	32.63	102.68	99.08	−66.45	218.72	212.37	253.64	247.29	−34.92
0.4	50.67	43.83	120.82	113.98	−70.15	225.58	218.69	279.50	272.61	−53.92
0.5	64.58	56.76	130.78	122.96	−66.20	218.38	210.43	283.58	275.63	−65.20
0.6	75.41	69.39	131.52	125.50	−56.11	202.21	192.67	268.09	258.55	−65.87
0.7	79.53	77.59	121.41	119.48	−41.88	177.89	166.85	233.67	222.62	−55.77
0.8	72.22	75.09	98.16	101.02	−25.94	141.94	130.74	179.42	168.23	−37.48
0.9	47.71	53.28	58.87	64.43	−11.15	86.53	78.50	102.87	94.84	−16.34

[a] All functions expressed as cal $gmol^{-1}$.

[b] Ethanol(1)–benzene(2).

[c] Benzene(1)–acetone(2).

[d] Carbontetrachloride(1)–acetone(2).

[e] Acetonitrile(1)–carbontetrachloride(2).

TABLE 8

CONSTANT VOLUME EXCESS THERMODYNAMIC FUNCTIONS[a] FOR BINARY MIXTURES IX AND X AT 45°C

X_1	IX^b					X^c				
	U_V^E	H_V^E	A_V^E	G_V^E	TS_V^E	U_V^E	H_V^E	A_V^E	G_V^E	TS_V^E
0.1	56.75	54.59	74.47	72.30	−17.72	155.92	171.24	135.33	150.65	+20.59
0.2	97.14	87.43	127.56	117.86	−30.43	229.70	248.34	220.48	239.12	+9.22
0.3	122.54	102.87	162.45	142.79	−39.91	248.95	263.94	267.56	282.55	−18.61
0.4	134.66	104.58	181.53	151.44	−46.87	236.14	243.24	286.06	293.15	−49.91
0.5	135.02	96.01	186.41	147.40	−51.39	207.84	205.41	282.87	280.43	−75.03
0.6	124.92	80.38	177.92	133.38	−53.00	174.68	163.49	262.28	251.09	−87.60
0.7	105.48	60.62	156.13	111.27	−50.65	141.37	124.40	225.95	208.98	−84.58
0.8	77.61	39.36	120.32	82.07	−42.71	106.75	88.89	172.93	155.06	−66.17
0.9	42.01	18.94	69.03	45.96	−27.01	63.77	51.54	99.66	87.42	−35.89

[a] All functions expressed as cal $gmol^{-1}$.

[b] Toluene(1)–acetonitrile(2).

[c] Ethanol(1)–toluene(2). For this system $T = 35$°C.

TABLE 9

COMPARISON OF MOLE FRACTION AVERAGE EXCESS THERMODYNAMIC FUNCTIONS[a] WITH EXPERIMENTAL VALUES FOR SYSTEM III[b] AT 45°C

X_1	U_V^E	$\overline{U_V^E}$[c]	H_V^E	$\overline{H_V^E}$	A_V^E	$\overline{A_V^E}$	G_V^E	$\overline{G_V^E}$	TS_V^E	$\overline{TS_V^E}$
0.1	52.53	52.91	29.05	29.12	62.53	62.53	39.05	38.74	−10.00	− 9.62
0.2	86.99	87.54	53.46	53.56	107.78	107.78	74.25	73.79	−20.78	−20.23
0.3	107.96	108.52	74.64	74.72	138.16	138.16	104.84	104.37	−30.20	−29.65
0.4	119.26	119.71	92.26	92.31	155.48	155.48	128.48	128.08	−36.22	−35.76
0.5	123.11	123.42	105.21	105.23	160.84	160.84	142.93	142.64	−37.72	−37.41
0.6	120.21	120.36	111.55	111.55	154.68	154.68	146.02	145.86	−34.47	−34.32
0.7	109.62	109.65	108.43	108.42	136.77	136.77	135.57	135.53	−27.14	−27.11
0.8	88.91	88.86	92.13	92.12	106.19	106.19	109.41	109.45	−17.28	−17.33
0.9	54.04	53.98	58.04	58.03	61.35	61.35	65.35	65.40	− 7.31	− 7.37

[a] All functions expressed as cal $gmol^{-1}$.

[b] Acetonitrile(1)-benzene(2).

[c] Overbar values computed by eqn (10).

TABLE 10

THERMAL PRESSURES[a] FOR TEN BINARY SYSTEMS AT 45°C

X_1	I[b]		II[c]		III[d]		IV[e]		V[f]	
	P_T	$\overline{P_T}$	P_T	$\overline{P_T}$	P_T	$\overline{P_T}$	P_T	$\overline{P_T}$	P_T	$\overline{P_T}$
0.1	3924	4019	3041	3009	3636	3768	3668	3848	3444	3711
0.2	3817	3877	3059	3027	3597	3732	3704	3900	3376	3619
0.3	3719	3749	3077	3045	3557	3692	3744	3958	3300	3525
0.4	3623	3637	3094	3062	3514	3649	3789	4021	3217	3426
0.5	3551	3438	3111	3080	3470	3604	3841	4093	3126	3324
0.6	3481	3479	3130	3099	3423	3556	3900	4176	3029	3217
0.7	3417	3375	3149	3120	3374	3506	3972	4276	2926	3105
0.8	3361	3307	3170	3142	3321	3453	4080	4405	2818	2987
0.9	3310	3246	3193	3167	3264	3396	4174	4583	2708	2863

X_1	VI[g]		VII[h]		VIII[i]		IX[j]		X[k]	
	P_T	$\overline{P_T}$	P_T	$\overline{P_T}$	P_T	$\overline{P_T}$	P_T	$\overline{P_T}$	P_T	$\overline{P_T}$[l]
0.1	3007	3059	2926	2983	2970	2941	3352	3310	3511	3406
0.2	3073	3129	2929	2976	2994	2966	3334	3288	3462	3362
0.3	3140	3202	2932	2967	3020	2994	3317	3267	3410	3314
0.4	3210	3278	2935	2959	3050	3026	3302	3249	3355	3263
0.5	3281	3357	2938	2951	3083	3061	3288	3232	3296	3208
0.6	3355	3439	2942	2945	3120	3101	3275	3218	3234	3150
0.7	3431	3524	2947	2938	3163	3146	3264	3206	3166	3088
0.8	3509	3613	2951	2933	3212	3198	3255	3198	3094	3022
0.9	3588	3704	2956	2927	3270	3259	3248	3193	3015	2950

[a] All values expressed in atm.

[b] Toluene(1)–nitroethane(2).

[c] Toluene(1)–acetone(2).

[d] Acetonitrile(1)–benzene(2).

[e] Nitromethane(1)–benzene(2).

[f] Ethanol(1)–benzene(2).

[g] Benzene(1)–acetone(2).

[h] Carbontetrachloride(1)–acetone(2).

[i] Acetonitrile(1)–carbontetrachloride(2).

[j] Toluene(1)–acetonitrile(2).

[k] Ethanol(1)–toluene(2). Temperature = 35°C.

[l] Overbar values computed by eqn (10).

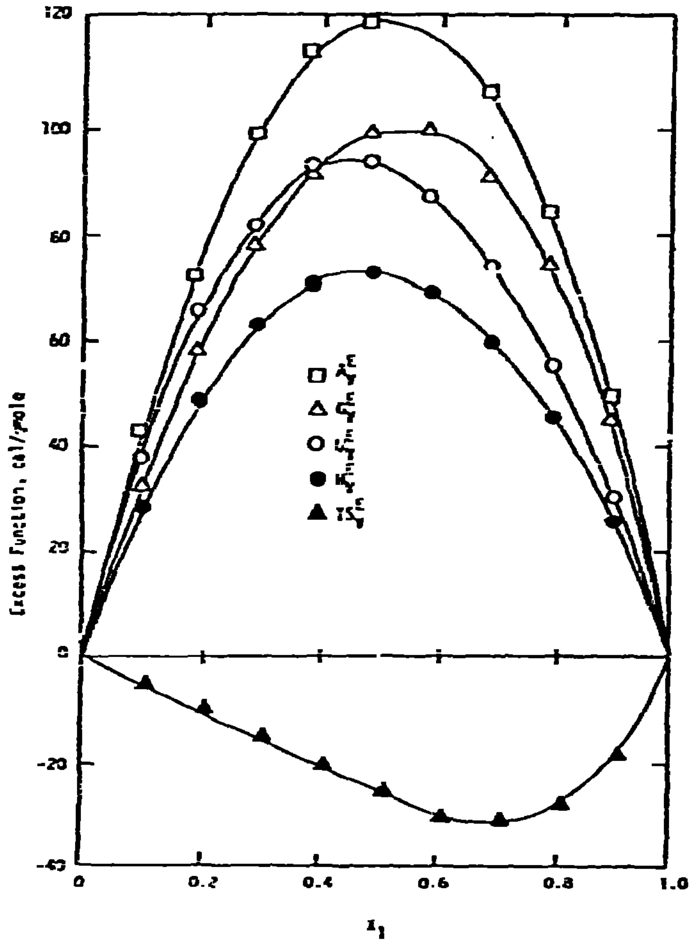

Fig. 4. Thermodynamic excess functions at constant volume for the toluene(1)–nitroethane(2) system at 45 °C.

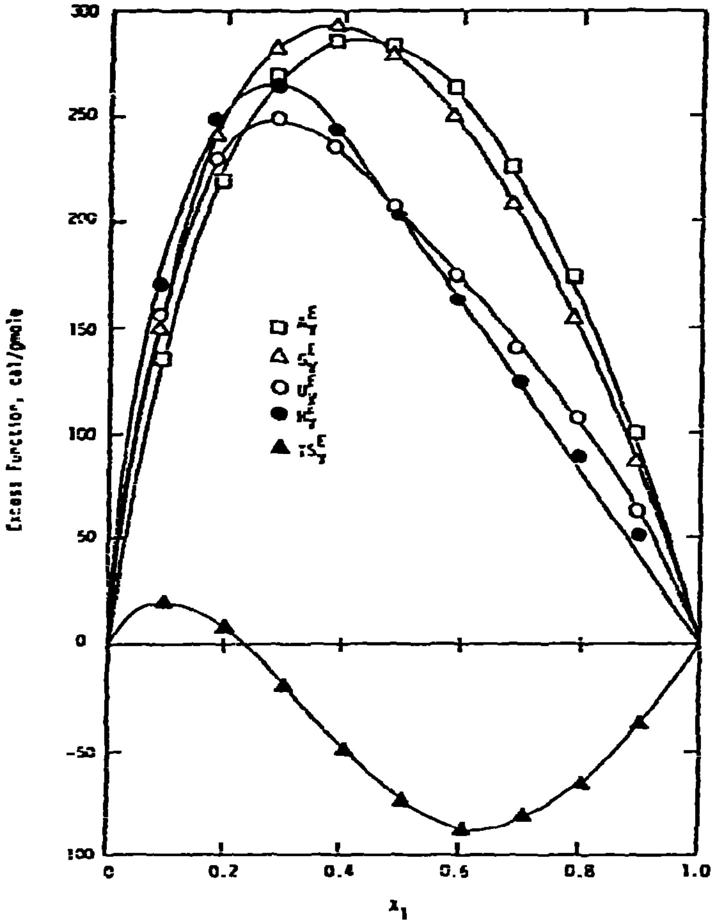

Fig. 5. Thermodynamic excess functions at constant volume for the ethanol(1)–toluene(2) system at 35°C.

is not quite as close as was observed between M_V^E and $\overline{M}_V^E$. However, for all of the systems except V, $\overline{P}_T$ agrees with P_T to within 2–3% on the average. For system V, $\overline{P}_T$ differs from P_T by 5–7% over the pressure range. These results suggest that for most purposes where P_T data would be needed, $\overline{P}_T$ should be an acceptable substitute for P_T.

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