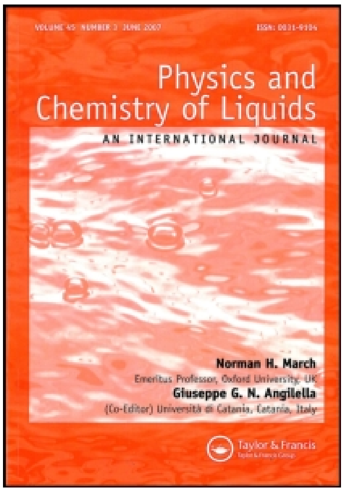

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Excess thermodynamic functions of some binary nonelectrolyte liquid mixtures. investigation of theory

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Excess Thermodynamic Functions of Some Binary Nonelectrolyte Liquid Mixtures. Investigation of Theory

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Theoretical predictions for excess thermodynamic functions obtained by utilizing a modified hard sphere equation of state are compared to existing experimental values for 14 binary liquid mixtures. Agreement with experimental values was found to be generally good, except in aromatic mixtures.

1. INTRODUCTION

The thermodynamic properties of a number of binary mixtures, differing from hard sphere nature have been investigated by utilizing the hard sphere equation of state of Reiss, Frisch, and Lebowitz[1] with a van der Waals attraction term, as used by Longuet-Higgins and Widom.[2] This equation of state, which has been successful when applied to mixtures involving a large globular molecule[3] and mixtures composed of small nonpolar molecules,[4] is applied to the case of binary mixtures differing significantly in size and shape.

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2. PURE COMPONENT EQUATION OF STATE

The equation of state can be written as

$$\frac{p}{\rho kT} = \phi(y) - \frac{a\rho}{kT}, \tag{1}$$

where p is the pressure, ρ is the number density, k is Boltzmann's constant, T is temperature, a is the van der Waals parameter, $\phi(y)$ is $(1 + y + y^2)/(1 - y)^3$, y is $1/6(\pi r^3 \rho)$, and r is the hard sphere diameter. The function of density $\phi(y)$ is the pressure of a hard sphere assembly at the same temperature and density as the model fluid.

3. EXCESS THERMODYNAMIC FUNCTIONS OF MIXING

The extension of equation (1) to binary mixtures follows from the work of Lebowitz[5] and is based on the generalization of $\phi(y)$ to a binary system and the configurational internal energy for mixing. The equation of the state for a binary mixture is

$$\frac{p}{\rho_m kT} = \phi_m(y_m,x) - \frac{(a_{11}\,x_1{}^2 + 2a_{12}\,x_1x_2 + a_{22}\,x_2{}^2)}{kT}\rho_m \tag{2}$$

where a_{11} and a_{22} are the pure components and a_{12} is the mixing parameter, ρ_m is the mixture density, x_1 and x_2 are the respective mole fractions, $\phi_m(y_m,x)$ is given by Snider and Herrington,[4] and y_m is $1/6(x_1 r_1{}^3 + x_2 r_2{}^3)\rho_m \pi$.

The respective equations for the excess functions are[4]

$$\frac{S^E}{Nk} = \sum_{i=1,2} x_i \left[\ln \frac{\rho_i(1-y_m)}{\rho_m(1-y_i)} + 3/2 \left(y_i \frac{2-y_i}{(1-y_i)^2} - y_m \frac{2-y_m}{(1-y_m)^2}\right)\right] \tag{3}$$

$$+ 3/2 \frac{y_m}{(1-y_m)^2} \frac{x_1x_2}{x_1r_1{}^3 + x_2r_2{}^3} (r_1 - r_2)^2 \left[2(r_1 + r_2) - y_m \frac{x_1r_1{}^4 + x_2r_2{}^4}{x_1r_1{}^3 + x_2r_2{}^3}\right] \tag{4}$$

$$\frac{H^E}{NkT} = \sum_{i=1,2} x_i \left\{\left[\frac{2p}{\rho_m kT} - \phi_m(y_m,x)\right] - \left[\frac{2p_i}{\rho_i kT} - \phi(y_i)\right]\right\} \; ; \tag{5}$$

and $G^E = H^E - TS^E$.

The excess volume is given by

$$V^E/N = \tfrac{1}{6}\pi \sum_{i=1,2} x_i r_i{}^2 \,(y_m^{-1} - y_i^{-1}). \tag{6}$$

4. CALCULATIONS

All of the parameters except a_{12} can be determined from experimental data. To determine a_{12} the excess Gibbs energy was forced to fit experimental data at a given temperature and composition. The experimental heat of vaporization and the molar volume are used to calculate the pure component parameters. Marsh[3] has used critical point data while Snider and Herrington[4] have used boiling point data.

Table 1 gives the necessary pure component data used in the calculations, while Table 2 lists the pure component parameters, where A and B refer to Equations (24) and (25) of Snider and Herrington. Calculated molar volumes are given in Table 3. Table 4 gives the calculated values for the selected excess functions.

TABLE 1

Boiling-point data for the pure components (atm = 101.325 kPa; $\mathrm{cal_{th}}$ = 4.184 J)

Substance	$\dfrac{\Delta Hv}{\mathrm{cal_{th}\ mol^{-1}}}$	$\dfrac{\rho^{-1}}{\mathrm{cm^3\ mol^{-1}}}$	$\dfrac{T}{K}$	$\dfrac{p}{atm}$
CH_4	$2035.9^{a,b}$	36.35	99.51	0.323
	2036.0^{c}	38.0	111.7	1
	1959.9^{d}	37.8	111.7	1
CF_4	$3007.1^{b,c}$	54.2	145.1	1
	3009.9^{d}	54.9	145.1	1
C_6H_6	$7353.0^{b,e}$	96.09^{f}	353.35^{e}	1
	7398.8^{g}	96	353.35	1
CCl_4	$7174.5^{a,b}$	103.74	349.81	1
c-C_6H_{12} (cyclohexane)	$7896.1^{b,o}$	108.75	298.15	0.128
C_7H_8 (toluene)	$7078.1^{b,l}$	$111.8{\pm}01^{n}$	333.15^{k}	0.185^{k}
C_6F_6	$8450.7^{b,h}$	116.614^{h}	303.15^{h}	0.141^{i}
	$7928.0^{g,j}$	122^{k}	333.41^{k}	0.500^{k}
$C(CH_3)_4$ (neopentane)	$5441.6^{a,b}$	119.67	282.66	1
p-C_8H_{10} (*p*-xylene)	$7710.7^{b,l}$	124.555^{k}	303.15^{k}	0.015^{k}
n-C_6H_{14}	$7046.2^{b,o}$	136.46	340.05	0.953
n-C_6F_{14}	$6700.0^{b,o}$	209.936	318.15	0.649
$(CH_3)_8Si_4O_4$ (octamethylcyclotetrasiloxane)	$9769.8^{b,l}$	339.56^{m}	346.55^{m}	0.026^{m}

TABLE 1

Boiling point data for the pure components (atm = 101.325 kPa; cal_{th} = 4.184 J), continued

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[a] From reference 4.

[b] Data used in calculations.

[c] From reference 9.

[d] From reference 10.

[e] From reference 11.

[f] From reference 12.

[g] From reference 13.

[h] From reference 14.

[i] From reference 7.

[j] Second set of data used in calculations.

[k] From reference 6.

[l] Estimated by the Watson relation.(15) See also reference 16. This estimation is within 0.5 per

[m] From reference 17.

[n] From reference 18.

[o] From reference 19.

Values of G^E for equimolar mixtures were forced to agree with experimental values at one temperature to fix a_{12} in all cases except the benzene + toluene, *p*-xylene systems where the value of V^E was used. The calculated results for the perfluorobenzene + aromatic systems differ significantly from the observed experimental values. Calculations were performed on these systems utilizing the experimental values of G^E and V^E, in addition to doing the calculations with a different set of pure component data for the perfluorobenzene + benzene system.

5. DISCUSSION

Since the excess properties are dependent upon the difference between unlike molecular behavior, the calculated results will be sensitive to the choice of mixing rules. A combining rule for a_{12} in the hard sphere model is[4]

$$a_{12} = (a_{11}\, a_{22} / r_1{}^3 r_2{}^3)^{1/2}\, [1/2(r_1 + r_2)]^3 . \tag{7}$$

Equation (7) is an empirical relation for small, nonpolar molecules.

From a comparison of the results obtained (Table 5) from equation (7) and equation (2) for the a_{12} parameter, it appears that the basic assumption of centrally symmetric molecular interactions is breaking down. This is especially evident in the case of the large molecules such that the range of intermolecular separation is small compared to the molecular diameter. For the system CCl_4 + $C(CH_3)_4$ the a_{12} calculated from equation (2) agrees well with the a_{12} calculated from equation (7) suggesting the validity of the model in this case.

The perfluorobenzene + aromatic mixtures are believed to form intermolecular complexes.[6] The strength of the complex increases with increasing methyl substitution. From Table 4 the excess functions calculated for these systems show increasing disagreement with experimental values with increasing methyl constituency. The onset of specific interactions causes the modified hard sphere model combining rules to be inapplicable. The c-C_6H_{12} + C_6F_6 system has been included as a non-complexing reference. Agreement between calculated and experimental excess functions is seen to be somewhat better for this system than the corresponding perfluorobenzene + aromatic mixtures. The lack of agreement between calculated and experimental excess functions for the c-C_6H_{12} + C_6F_6 mixture can be attributed to the unusual weakness of the physical interactions

TABLE 2

Parameters for the pure components (Å = 0.1 nm)

Substance	Method (A)		Method (B)	
	r / Å	a × 10^{-5} / J cm^3 mol^{-1}	r / Å	a × 10^{-5} / J cm^3 mol^{-1}
CH_4	3.68_5	2.69	3.70_2	2.80
CF_4	4.39_6	8.77	4.23_6	6.17
C_6H_6	5.28_6	35.56	5.13_1	26.88
CCl_4	5.40_6	36.67	5.25_2	28.12
c-C_6H_{12} (cyclohexane)	5.65_4	44.88	5.49_9	33.23
C_7H_8	5.51_3	36.15	5.46_5	33.22
C_6F_6	5.88_2	59.76	5.65_9	38.29
	5.87_5[a]	56.37[a]	5.64_5[a]	37.08[a]
$C(CH_3)_4$ (neopentane)	5.62_0	31.41	5.46_3	24.44
p-C_8H_{10} (p-xylene)	5.70_2	35.48	5.78_2	40.67
n-C_6H_{14}	5.98_6	52.31	5.76_3	36.37
n-C_6F_{14}	6.97_0	82.55	6.66_7	53.29
$(CH_3)_8Si_4O_4$ (octamethyltetrasiloxane)	8.30_7	173.31	8.09_0	129.01

[a] Calculated from second set of boiling-point data

TABLE 3

Molar volumes of the pure components

		Molar volume/ $cm^3\ mol^{-1}$		
Substance	$\frac{T}{K}$	expt.	Method (A)	Method (B)
CH_4	106.7	37.17[j]	37.89	37.83
CF_4	106.7	48.93[j]	48.71	47.30
C_6H_6	273.15	86.78[d]	87.24	85.44
	298.15	89.41[b]	89.43	88.56
	300.15	89.65[c]	89.89	88.81
	303.15	89.89[a]	90.11	89.68
	313.15	91.12[c]	91.51	90.50
CCl_4	273.15	94.23[d]	94.44	92.56
	298.15	97.09[b]	97.41	96.04
	300.15	97.32[c]	97.65	96.31
	313.15	98.91[c]	99.22	98.20
c-C_6H_{12} (cyclohexane)	298.15	108.68[e]	108.81	108.81
	303.15	109.41[f]	109.44	109.60
C_7H_8 (toluene)	313.15	108.60[g]	108.66	108.24
C_6F_6	303.15	116.61[i]	116.68	116.72
	313.15	118.00[h]	117.86	118.26
$C(CH_3)_4$ (neopentane)	273.15	117.97[d]	117.90	117.51
p-C_8H_{10} (p-xylene)	313.15	126.80[g]	126.51	126.34
n-C_6H_{14}	308.15	133.35[k]	131.52	130.02
n-C_6F_{14}	308.15	205.91[l]	206.57	206.75
$(CH_3)_8Si_4O_4$ (octamethyltetrasiloxane)	298.15	312.10[b]	324.16	320.87

[a] From reference 20.

[b] From reference 21.

[c] From reference 38.

[d] From reference 22.

[e] From reference 23.

[f] From reference 4.

[g] From reference 24.

[h] From reference 6.

[i] From reference 14.

[j] From reference 9.

[k] From reference 25.

[l] From reference 19.

TABLE 4

Excess functions for equimolar mixtures ($cal_{th} = 4.184$ J)

Mixture	$\frac{T}{K}$	$G^E/cal_{th}\ mol^{-1}$			$H^E/cal_{th}\ mol^{-1}$		
		Method (A)	Method (B)	expt.	Method (A)	Method (B)	expt.
n-C_6H_{14} + n-C_6F_{14}	308.15	--	--	318[o]	501	503	567 ± 20[o]
c-C_6H_{12} + C_6F_6	303.15	--	--	191.44[n]	271	299	368.78[n]
C_6H_6 + $C(CH_3)_4$	273.15	--	--	158[f]	188	203	--
CH_4 + CF_4	106.7	--	--	86[k]	114	112	(119)[l]
							(116)[m]
CCl_4 + $C(CH_3)_4$	273.15	--	--	78.5[f]	84	89	75 ± 5[g]
C_6H_6 + c-C_6H_{12}	298.15	--	--	74.4[b]	107	113	175.8[b]
	303.15	--	--	70[a]	101	107	170[a]
$(CH_3)_8Si_4O_4$ + C_6H_6	298.15	--	--	27.7[i,j]	287	277	178.1[i,j]
C_6H_6 + CCl_4	298.15	--	--	20[c]	27	29	27[d]
	313.15	--	--	19[c]	27	30	30 ± 1[e]
C_6H_6 + C_6F_6	313.15	--	--	−10.5[h]	−14	−5	−103.97[h]
C_6H_6 + C_6F_6[p]	313.15	−166.18	−99.28	−10.5[h]	−74	−35	−103.97[h]
C_6H_6 + C_6F_6[t]	313.15	--	--	−10.5[h]	−7	−4	−103.97[h]
$(CH_3)_8Si_4O_4$ + CCl_4	298.15	--	--	−31.8[i]	173	167	--
C_7H_8 + C_6F_6	313.15	--	--	−44.22[h]	−93	−62	−259.32[h]
C_7H_8 + C_6F_6[p]	313.15	−297.44	−91.76	−44.22[h]	−197	−56	−259.32[h]

TABLE 4

Excess functions for equimolar mixtures ($cal_{th} = 4{,}184$ J), continued

		G^E/cal_{th} mol^{-1}			H^E/cal_{th} mol^{-1}		
Mixture	$\frac{T}{K}$	Method (A)	Method (B)	expt.	Method (A)	Method (B)	expt.
$p\text{-}C_8H_{10} + C_6F_6$	313.15	--	--	-93.69^{h}	-201	-133	-396.75^{h}
$p\text{-}C_8H_{10} + C_6F_6$	313.15	-189.39	130.86	-93.69^{h}	-89	-53	-396.75^{h}
$C_6H_6 + C_7H_8{}^{p}$	288.15	-354.72	-385.57	--	9	2	14.98^{q}
$C_6H_6 + p\text{-}C_8H_{10}{}^{p}$	298.15	-346.88	-386.98	--	106	57	38.98^{r}
		S^E/cal_{th} K^{-1} mol^{-1}			V^E/cm^3 mol^{-1}		
$n\text{-}C_6H_{14} + n\text{-}C_6F_{14}$	308.15	0.59	0.60	0.80	11.58	3.47	5.39^{o}
$c\text{-}C_6H_{12} + C_6F_6$	303.15	0.26	0.35	0.58	0.50	1.67	2.56^{n}
$C_6H_6 + C(CH_3)_4$	273.15	0.11	0.16	--	-1.06	-0.89	-0.514^{f}
$CH_4 + CF_4$	106.7	0.26	0.23	0.31^{v}	0.40	0.27	0.88^{k}
$CCl_4 + C(CH_3)_4$	273.15	0.02	0.04	-0.01^{c} ±0.02	-0.96	-1.01	-0.525^{f}
$C_6H_6 + c\text{-}C_6H_{12}$	298.15	0.11	0.13	0.34	0.27	0.40	0.65^{b}
	303.15	0.10	0.12	0.32	0.26	0.39	0.652^{a}
$(CH_3)_8Si_4O_4 + C_6H_6$	298.15	0.87	0.84	$0.51^{i,j}$	-0.68	-0.03	$-0.007^{i,j}$

Excess functions for equimolar mixtures ($cal_{th} = 4.184$ J), continued

Mixture	$\frac{T}{K}$	$S^E/cal_{th}\ K^{-1}\ mol^{-1}$ Method (A)	Method (B)	expt.	$V^E/cm^3\ mol^{-1}$ Method (A)	Method (B)	expt.
$C_6H_6 + CCl_4$	298.15	0.02	0.03	0.03[b]	0.03	0.08	0.01[d]
	313.15	0.03	0.03	0.03[b]	0.03	0.08	0.04[d]
$C_6H_6 + C_6F_6$	313.15	–0.01	–0.02	–0.298	–0.21	–0.03	0.763[u]
$C_6H_6 + C_6F_6$[p]	313.15	0.26	0.21	–0.298	––	––	0.763[h]
$C_6H_6 + C_6F_6$[t]	313.15	0.01	0.02	–0.298	0.01	0.02	0.763[h]
$(CH_3)_8Si_4O_4 + CCl_4$	298.15	0.69	0.67	––	–0.12	–0.14	–0.254[i]
$C_7H_8 + C_6F_6$	313.15	–0.16	–0.06	–0.687	–0.91	–0.28	0.42[h]
$C_7H_8 + C_6F_6$[p]	313.15	0.32	0.11	–0.687	––	––	0.42[h]
p-$C_8H_{10} + C_6F_6$	313.15	–0.34	–0.12	–0.968	–2.81	–0.63	0.09[h]
p-$C_8H_{10} + C_6F_6$	313.15	0.32	0.25	–0.968	––	––	0.09[h]
$C_6H_6 + C_7H_8$[f]	288.15	1.61	1.37	––	––	––	0.093[q]
C_6H_6 + p-C_8H_{10}[f]	298.15	1.52	1.49	––	––	––	0.213[r]

[a] From reference 26.
[b] From reference 27.
[c] Derived from experimental values for excess enthalpy and excess entropy.
[d] From reference 28.
[e] From reference 29.
[f] From reference 22.
[g] From reference 30.
[h] From reference 31.
[i] From reference 21.
[j] Values are expected to apply more accurately at 42.5 °C (see reference 21).
[k] From reference 32.
[l] From reference 33. An estimated value.
[m] From reference 34. A calculated value.
[n] From reference 7.
[o] From reference 25.
[p] Employing the experimental V^E as a fixed parameter.
[q] From reference 35.
[r] From reference 36.
[s] From reference 37.
[t] Using the second set of data indicated under boiling-point data, fixing G^E.
[u] From reference 24.
[v] Derived from experimental values for excess Gibbs energy and excess enthalpy.

TABLE 5

Values of the parameter a_{12}

		$a_{12} \times 10^{-5}$ /J cm^3 mol^{-1}			
		From A set of parameters		From B set of parameters	
Mixtures	$\frac{T}{K}$	Using expt. G^E	Using eq. (7)	Using expt. G^E	Using eq. (7)
$C_6H_6 + CCl_4$	298.15	35.89	36.12	27.29	26.88
	313.15	35.90		27.30	
$C_6H_6 + c\text{-}C_6H_{12}$	298.15	39.27		29.27	
	303.15	39.31	40.02	29.30	29.94
$C_6H_6 + C(CH_3)_4$	273.15	33.24	33.47	25.13	25.67
$CCl_4 + C(CH_3)_4$	273.15	34.01	33.96	26.05	26.23
$C_6H_6 + C_6F_6$	313.15	45.89	46.30	32.15	32.20
$(CH_3)_8Si_4O_4 + C_6H_6$	298.15	82.81	84.70	61.74	63.60
$CCl_4 + (CH_3)_8Si_4O_4$	298.15	84.03	85.39	63.29	64.56
$CH_4 + CF_4$	106.7	7.25	4.91	3.86	4.18
$C_7H_8 + C_6F_6$	313.15	38.80	42.46	30.16	31.22
$p\text{-}C_8H_{10} + C_6F_6$	313.15	43.70	47.06	28.09	30.20
$n\text{-}C_6H_{14} + n\text{-}C_6F_{14}$	308.15	45.09	65.52	40.19	44.38
$C_6F_6 + c\text{-}C_6H_{12}$	303.15	48.89	51.82	33.15	35.68
$C_7H_8 + C_6H_6$[a]	288.15	39.07	32.67	34.27	26.12
$p\text{-}C_8H_{10} + C_6H_6$[a]	298.15	32.97	36.38	39.69	25.33

[a] Using experimental V^E.

occuring in the system. It has been found that the energy of unlike interactions is about 5 percent weaker than the value predicted by the geometric mean rule for this system.[7]

The size effect for molecular systems is directly incorporated into the equation of state for the modified hard sphere model considered here and is a particularly strong feature of this model, as can be seen from a comparison of the systems: $CCl_4 + (CH_3)_8Si_4O_4$, $C_6H_6 + (CH_3)_8Si_4O_4$, $n\text{-}C_6H_{14} + n\text{-}C_6F_{14}$, and $CH_4 + CF_4$. Shape does not appear to be as important a factor as energy and size in the $n\text{-}C_6H_{14} + n\text{-}C_6F_{14}$ mixture.[8] Agreement between calculated and experimental values for these systems is good, indicating large differences in molecular size are being accounted for reasonably well.

The systems $C_6H_6 + C_7H_8$, $C_6H_6 + p\text{-}C_8H_{10}$ are of approximately similar symmetry and size. However, agreement between calculated and experimental excess values for these systems is only slightly better than the perfluorobenzene + aromatic mixtures suggesting specific interactions are causing the observed deviations.

For systems composed of molecules of dissimilar type but of approximately equal size, C_6H_6 + c-C_6H_{12}, C_6H_6 + CCl_4, agreement between calculated and experimental excess values is good.

The success of this model in reproducing experimental values of various thermodynamic quantities for the pure substances and for the mixtures, when nonspecific and specific interactions are not apparent, is good in view of the fact the molecules considered in this work differ significantly from sphericity and is indicative of the superiority of the model when size differences are large.

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