Semiempirical equation for the excess volumes in simple liquid mixtures and polymer solutions

S. Saeki, M. Tsubokawa, J. Yamanaka and T. Yamaguchi
Department of Materials Science and Engineering, Fukui University, Fukui 910, Japan

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A semiempirical equation for the excess volume Δv_m in simple liquid mixtures such as Ar–N_2, methane–ethane and benzene–cyclohexane, and polymer solutions such as polyisobutylene–benzene and polystyrene–cyclohexane, has been derived based on the experimental data of Δv_m for simple liquid mixtures by Calado *et al.* and Rabio *et al.* and for polymer solutions by Flory *et al.* and Patterson *et al.* The expression for the specific volume of mixtures v_m obtained in this work is given by

$$v_m = v_0^\circ (v_1^\circ / v_0^\circ)^{Y(x_1)}$$

where

$$Y(x_1) = [2^n/(2^n - 1)] - [(2 - x_1)^n (2^n - 1)^{-1}]$$

and where v_0° and v_1° are the specific volumes of solvent (0) and solute (1), respectively, in the pure state, x_1 is the mole fraction of solute (1) and $n(\neq 0)$ is a function of temperature and pressure. Values of n at 1 atm and 20–25°C for various mixtures including polymer solutions range from -1.1 to 5.5. It is found that Δv_m is negative for mixtures with $v_1^\circ/v_0^\circ < 1$, while $\Delta v_m > 0$ for $v_1^\circ/v_0^\circ > 1$ in most simple mixtures except for polymer solutions with $\Delta v_m > 0$.

(Keywords: excess volume; simple liquid mixture; polymer solution; semiempirical equation; specific volume of mixture)

INTRODUCTION

The excess volume Δv_m is an important quantity in characterizing solution properties of mixtures and its theoretical prediction has been extensively carried out in simple liquid mixtures and polymer solutions. Calado *et al.*[1–5] and Machado *et al.*[6] have investigated Δv_m for mixtures containing Kr, Xe, methane and hydrogen chloride to develop a molecular theory of solutions including systems showing multipolar interactions. Nakata and Sakurai[7] have investigated the relationship between excess refractive index and excess volume. Flory *et al.* have derived the equation of state for liquids and liquid mixtures and applied it to simple liquid mixtures and polymer solutions[8–20]. An investigation of Δv_m in mixtures containing branched and cycloalkanes and fluoro- and chlorocarbon has been carried out by Rubio *et al.*[21–24]. Patterson and Bardin have tested the Prigogine theory of corresponding states based on the experimental data for n-alkane mixtures[25]. Theoretical studies on simple mixtures have been carried out by Streett and Staveley[26], Leonard *et al.*[27], Longuet-Higgins[28], Snider and Herrington[29], Leland *et al.*[30] and Rowlinson and Swinton[31,32].

In this study we have derived a semiempirical equation for the excess volume or specific volume for mixtures based on essentially the same mathematical procedure as that used for deriving an equation of state[33].

DERIVATION OF SEMIEMPIRICAL EQUATION FOR SPECIFIC VOLUME AND EXCESS VOLUMES IN MIXTURES

It is assumed that a specific volume of mixture is expressed by

$$v_m = a_0(T, P)(\partial v_m/\partial n_0)_{T,P,n_1} n_0 f(n_0, n_1, T, P) \quad (1)$$

where $a_0(T, P)$ is a function of temperature and pressure, n_0 and n_1 are the number of molecules of solvent (0) and solute (1), respectively, and $f(n_0, n_1, T, P)$ is a function of n_0, n_1, T and P. It is useful to introduce the mole fraction for a simple liquid mixture:

$$x_i = n_i/(n_0 + n_1) \quad (2)$$

and the volume fraction for a polymer solution:

$$\phi_i = n_i \bar{v}_i^\circ/(n_0 \bar{v}_0^\circ + n_1 \bar{v}_1^\circ) = x_i V_i^\circ/(x_0 V_0^\circ + x_1 V_1^\circ) \quad (3)$$

where $\bar{v}_i^\circ$ is a molecular volume of component i and V_i° is the molar volume. Equation (1) can be rewritten using equation (2):

$$v_m = a_0(T, P)(\partial v_m/\partial x_0)_{T,P,n_1} x_0 x_1 f(n_0, n_1, T, P) \quad (4)$$

and a similar equation is derived from equations (1) and (3):

$$v_m = a_0(T, P)(\partial v_m/\partial \phi_0)_{T,P,n_1} \phi_0 \phi_1 f(n_0, n_1, T, P) \quad (5)$$

Equations (4) and (5) are essentially the same and the

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following derivation is carried out for equation (4).

By taking the derivative of equation (4) with respect to x_0:

$$(\partial v_m/\partial x_0)_{T,P,n_1} = a_0(\partial^2 v_m/\partial x_0^2)x_1x_0f + a_0(\partial v_m/\partial x_0)(x_1 - x_0)f + a_0(\partial v_m/\partial x_0)x_0x_1(\partial f/\partial x_0) \quad (6)$$

By dividing equation (6) by $a_0(\partial v_m/\partial x_0)x_0x_1f$:

$$(a_0x_0x_1f)^{-1} = (\partial^2 v_m/\partial x_0^2)/(\partial v_m/\partial x_0) + x_0^{-1} - x_1^{-1} + (\partial f/\partial x_0)/f \quad (7)$$

By integrating equation (7) with respect to x_0 from 0 to x_1:

$$(\partial v_m/\partial x_0) = (x_0x_1f)^{-1}c_0 \times \exp\left\{a_0^{-1}\int_0^{x_1}[\mathrm{d}x_0/(x_0x_1f)]\right\} \quad (8)$$

The specific volume of the mixture v_m is obtained using equations (4) and (8):

$$v_m = a_0c_0\exp\left\{a_0^{-1}\int_0^{x_1}[\mathrm{d}x_0/(x_0x_1f)]\right\} \quad (9)$$

The following simple equation is derived using the conditions that $v_m(x_0 = 0) = v_1^\circ$ and $v_m(x_0 = 1) = v_0^\circ$:

$$v_1^\circ = a_0c_0\exp a_0^{-1}\int_0^1[\mathrm{d}x_0/(x_0x_1f)] \quad (10)$$

and

$$v_0^\circ = a_0c_0 \quad (11)$$

From equations (10) and (11):

$$a_0^{-1} = \ln(v_1^\circ/v_0^\circ)\Big/\int_0^1[\mathrm{d}x_0/(x_0x_1f)] \quad (12)$$

The final expression for v_m is:

$$v_m = v_0^\circ\exp Y(x_0, T, P)\ln(v_1^\circ/v_0^\circ) = v_0^\circ(v_1^\circ/v_0^\circ)^{Y(x_0,T,P)} \quad (13)$$

where

$$Y(x_0, T, P) = \int_0^{x_1}[\mathrm{d}x_0/(x_0x_1f)]\Big/\int_0^1[\mathrm{d}x_0/(x_0x_1f)] \quad (14)$$

The excess volume Δv_m using equation (13) is given by:

$$\Delta v_m = v_m - w_0v_0^\circ - w_1v_0^\circ \quad (15)$$

$$= v_0^\circ(v_1^\circ/v_0^\circ)^{Y(x_0,T,P)} - w_0v_0^\circ - w_1v_1^\circ \quad (16)$$

where w_1 is the weight fraction $[w_i = m_i/(m_0 + m_1)$, where m_i is the mass of component $i]$.

METHOD OF ANALYSING EXPERIMENTAL DATA OF ΔV_M

The experimental data published for the excess volume or volume of mixtures are given by various expressions such as ΔV_M (cm^3 mol^{-1}) and $\Delta V_M/V^\circ$, which must be converted to v_m (cm^3 g^{-1}) to examine the equations in this study. The conversion was carried out using the following equations:

$$v_m = V_M/(x_0M_0 + x_1M_1) = \Delta V_M/(x_0M_0 + x_1M_1) + w_0v_0^\circ + w_1v_1^\circ \quad (17a)$$

and

$$v_m = (1 + \Delta v_{m_0}/v^\circ)/(\phi_0/v_0^\circ + \phi_1/v_1^\circ) \quad (17b)$$

where $v^\circ = w_0v_0^\circ + w_1v_1^\circ$.

It is important to determine the functions Y or f in equation (14). It is pointed out by equation (8) that the function f must be expressed by $f^{-1} = x_0x_1h(x_0, T, P)$ to avoid divergence of $(\partial v_m/\partial x_0)$ at the limit of $x_0 \to 0$ and $x_1 \to 0$ and by equation (14) that $Y(x_0 = 0) = 1.0$ and $Y(x_0 = 1.0) = 0$. The expression for $Y(x_0)$ is given by:

$$Y(x_0, T, P) = \int_0^{x_1} h(x_0, T, P)\,\mathrm{d}x_0\Big/\int_0^1 h(x_0, T, P)\,\mathrm{d}x_0 \quad (18)$$

where $h(x_0, T, P)$ is a function of x_0, T and P. One of the simplest expressions which satisfies the above conditions is:

$$Y(x_0) = -a(2 - x_1)^n + b \qquad n \neq 0 \quad (19)$$

where $a = (2^n - 1)^{-1}$, $b = 2^n/(2^n - 1)$ and n is a function of T and P.

It is of particular interest to find the determining factors for the sign of Δv_m. It is well known that the sign of the second derivative of v_m with respect to concentration $(\partial^2 v_m/\partial x_0^2)$ is negative for $\Delta v_m > 0$, while it is positive for $\Delta v_m < 0$. The expression for $(\partial^2 v_m/\partial x_i^2)$ calculated by equation (13) is given by:

$$(\partial^2 v_m/\partial x_0^2) = v_m[\ln(v_1^\circ/v_0^\circ)](\partial Y/\partial x_0)^2 \times [\ln(v_1^\circ/v_0^\circ) + (\partial^2 Y/\partial x_0^2)/(\partial Y/\partial x_0)^2] \quad (20)$$

where two factors, $\ln(v_1^\circ/v_0^\circ)$ and the second term in the square brackets in equation (20), determine the sign of Δv_m. Evaluation of the second term is done using equation (19):

$$-(\partial^2 Y/\partial x_0^2)/(\partial Y/\partial x_0)^2 = (2^n - 1)(n - 1)/[n(2 - x_1)^n] \quad (21)$$

The lines satisfying $(\partial^2 v_m/\partial x_0^2) = 0$ are calculated by equations (20) and (21) with $x_1 = 0.5$ (*Figure 1*). It is estimated from equation (20) that regions I and III in *Figure 1* correspond to $(\partial v_m^2/\partial x_0^2) < 0$ or $\Delta v_m > 0$, while regions II and IV correspond to $(\partial^2 v_m/\partial x_0^2) > 0$, $\Delta v_m < 0$.

RESULTS

The experimental data for ΔV_M and V_M published by many authors are analysed based on the equations in this work [equations (13), (17) and (19)]. *Figure 1* plots n *versus* v_1°/v_0° and lines for distinguishing $\Delta v_m > 0$ from $\Delta v_m < 0$ calculated using equation (20) are also shown. Values of n in this work are obtained by the best fit with data for Δv_m at a concentration such as $x_1 = 0.5$ and for $\Delta v_m = 0$ at $x_1 = 0$ and 1.0. Values for n, v_1°/v_0°, ΔV_M (observed) and V_c are given in *Tables 1–4*. A good prediction for the sign of Δv_m is obtained using equation (13) for all regions. (All data from the references are not used because in some cases there is no information on v_i° and in some mixtures V_c is unknown[39,40,43–45,47,48].)

It is very important to discuss how to determine and distinguish a solute from a solvent in a mixture, particularly in a simple liquid mixture such as Ar–O_2 or C_2H_6–C_2H_4. In this work we have taken a solute which

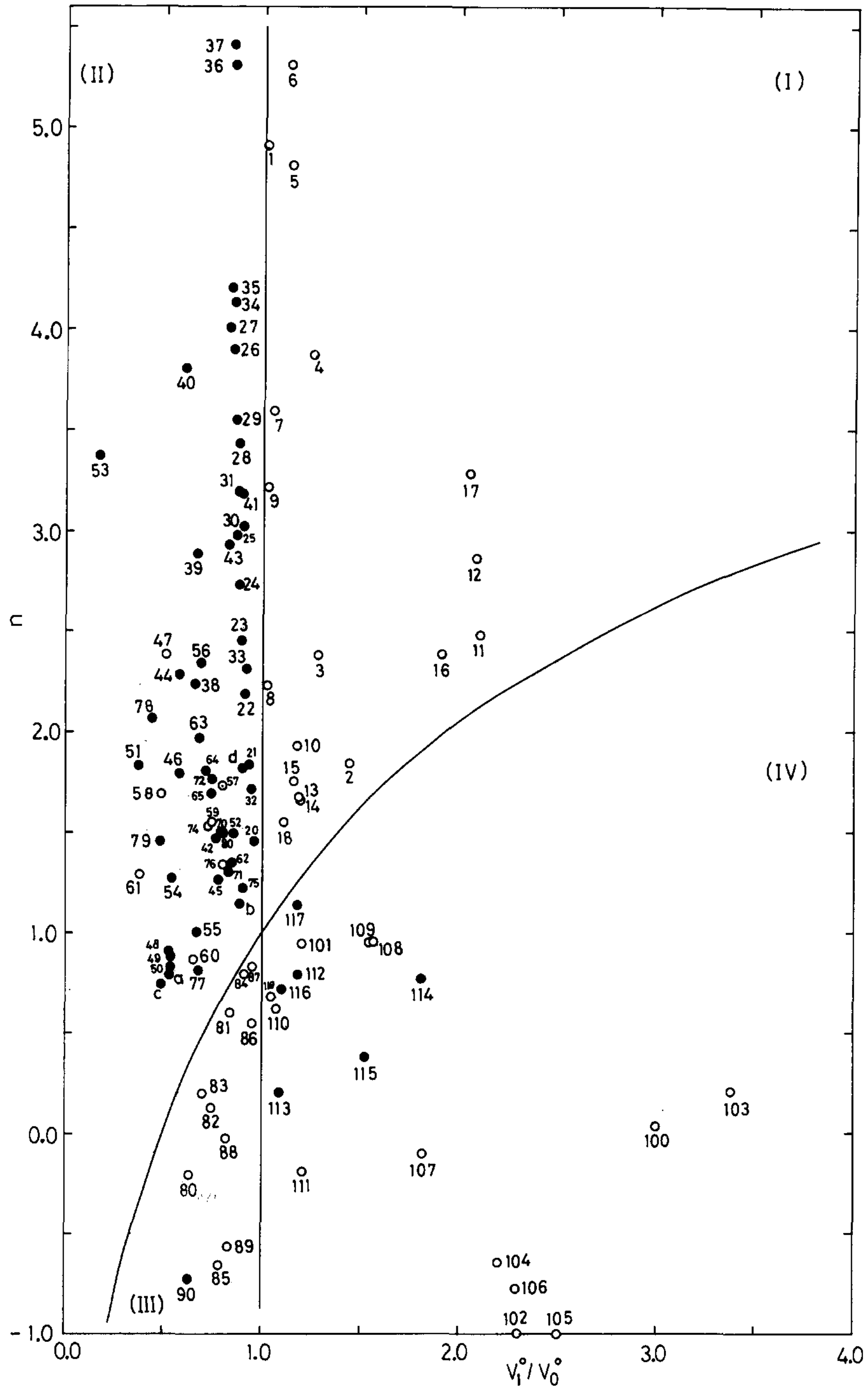

Figure 1 Plot of n *versus* v_1°/v_0° for the various mixtures indicated in *Tables 1–4*. The values of n are determined from experimental data and equations (13) and (19): (○) systems with $\Delta v_M > 0$; (●) systems with $\Delta v_M < 0$. The solid lines are calculated using equations (20) and (21) with $x_1 = 0.5$ and indicate that regions I and III are $\Delta v_M > 0$, while regions II and IV are $\Delta v_M < 0$

has a larger value for V_c/V in the pure state than that of the other component. The term V_c/V gives the number of molecules within the critical volume V_c where V_c is a measure of the effective range of interaction for a molecule at the centre of V_c. Therefore, a liquid with a large V_c/V is a dense liquid compared to that with small V_c/V and is diluted if it is mixed with the liquid with small V_c/V. The former liquid has the characteristic properties of a solute and the latter has those of a solvent.

It is interesting to point out from equation (20) that Δv_m is zero for a system with $v_1^\circ/v_0^\circ = 1.0$, which leads to the obvious and reasonable result that $\Delta v_m = 0$ when a liquid is mixed with the same liquid. The nearest value of v_1°/v_0° to 1.0 observed in this work is $v_1^\circ/v_0^\circ = 1.020$ in p-xylene–C_6H_6 where Δv_m ($cm^3\ g^{-1}$) $= 2.24 \times 10^{-3}$. It is also found that values of n depend slightly on temperature as shown in *Tables 1–4*. For example, n for n-$C_{16}H_{34}$– n-C_8H_{18} is 3.02 at 293 K and 3.19 at 379 K. It is also interesting to examine what happens if the definitions for solute and solvent are exchanged. The values of n then shift to new positions which are opposite and symmetrical with respect to the point (1, 1) in *Figure 1*. Therefore most of the points shift to a new region with the same sign of Δv_m such as I↔III and II↔IV (*Figure 1*).

Table 1 Excess volume of mixing Δv_m in region I

Solute (1)	M_w (g mol^{-1})	v_1° (cm^3 g^{-1})	V_c/V_1°	Solvent (0)	M_w (g mol^{-1})	v_0° (cm^3 g^{-1})	V_c/V_0°	T (K)	v_1°/v_0°	$\Delta V_m(x_1)_{obs.}$ (cm^3 mol^{-1})	n	No. (point)	Ref.
C_2H_6	30.070	1.7475	2.816	C_2H_4	28.054	1.7279	2.661	161.4	1.0113	0.153(0.464)	4.91	1	5
C_6H_6	78.114	1.1445	2.897	CS_2	76.131	0.7962	2.805	298	1.438	0.526(0.5)	1.84	2	32
n-C_7H_{16}	100.205	1.4721	2.928	C_6H_6	78.114	1.1445	2.897	298	1.2862	0.62 (0.5)	2.38	3	9
n-C_8H_{18}	163.541	1.4317	3.008	C_6H_6	78.114	1.1445	2.897	298	1.2509	0.73 (0.5)	3.87	4	23
n-$C_{14}H_{30}$	198.394	1.3106		C_6H_6	78.114	1.1445	2.897	298	1.1450	1.10 (0.5)	4.81	5	22
n-$C_{16}H_{34}$	226.448	1.2992		C_6H_6	78.114	1.1445	2.897	298	1.1351	1.17 (0.5)	5.31	6	22
cyc.-C_8H_{16}	112.216	1.2018		C_6H_6	78.114	1.1445	2.897	298	1.0515	0.586(0.5)	3.59	7	23
CH_3-C_6H_5	92.141	1.1726	2.925	C_6H_6	78.114	1.1578	2.864	308	1.0128	0.074(0.5)	2.23	8	49
p-Xylene	106.168	1.1674	3.058	C_6H_6	78.114	1.1445	2.897	298	1.020	0.207(0.499)	3.22	9	38
n-C_7H_{16}	100.205	1.4629	2.947	cyc.-C_6H_{12}	84.162	1.2844	2.849	293	1.1806	0.30 (0.5)	1.93	10	9
n-$C_{14}H_{30}$	198.394	1.3106		C_6F_6	186.056	0.6228		298	2.1043	2.13 (0.5)	2.48	11	22
n-$C_{16}H_{34}$	226.448	1.2992		C_6F_6	186.056	0.6228		298	2.086	2.19 (0.5)	2.86	12	22
m-Xylene	106.168	1.1574	3.0599	Aniline	93.129	0.9783	2.963	293	1.1829	0.064(0.548)	1.67	13	41
p-Xylene	106.168	1.1614	3.0736	Aniline	93.129	0.9783	2.963	293	1.1870	0.030(0.486)	1.66	14	41
o-Xylene	106.168	1.1364	3.0584	Aniline	93.129	0.9783	2.963	293	1.1615	0.172(0.472)	1.75	15	41
n-C_6H_{14}	86.178	1.5267	2.812	CS_2	76.131	0.7962	2.805	298	1.917	0.248(0.5)	2.38	16	32
n-$C_{16}H_{34}$	226.448	1.2932		CCl_4	153.823	0.6312	2.843	298	2.049	0.67 (0.5)	3.29	17	32
cyc.-C_8H_{16}	112.216	1.2018		ClC_6H_5	112.559	0.9083	3.012	298	1.1104	0.395(0.48)	1.55	18	23

Table 2 Excess volume of mixing Δv_m in region II

Solute (1)	M_w (g mol^{-1})	v_1° (cm^3 g^{-1})	V_c/V_1°	Solvent (0)	M_w (g mol^{-1})	v_0° (cm^3 g^{-1})	V_c/V_0°	T (K)	v_1°/v_0°	$\Delta V_m(x_1)_{obs.}{}^a$ (cm^3 mol^{-1})	n	No. (point)	Ref.
n-C_7H_{16}	100.205	1.4721	2.928	n-C_6H_{14}	86.178	1.5267	2.812	298	0.96423	−0.023 (0.5)	1.45	20	50
n-C_8H_{18}	114.232	1.4225	3.027	n-C_6H_{14}	86.178	1.5267	2.812	298	0.9317	−0.082 (0.5)	1.83	21	50
n-C_9H_{20}	128.259	1.3928	3.068	n-C_6H_{14}	86.178	1.5267	2.812	298	0.9123	−0.149 (0.5)	2.18	22	50
n-$C_{10}H_{22}$	142.286	1.3699	3.094	n-C_6H_{14}	86.178	1.5267	2.812	298	0.8973	−0.225 (0.6)	2.45	23	50
n-$C_{11}H_{24}$	156.313	1.3514	3.125	n-C_6H_{14}	86.178	1.5267	2.812	298	0.8852	−0.294 (0.6)	2.73	24	50
n-$C_{12}H_{26}$	170.340	1.3369		n-C_6H_{14}	86.178	1.5267	2.812	298	0.8757	−0.35 (0.6)	2.98	25	50
n-$C_{16}H_{34}$	226.448	1.2937		n-C_6H_{14}	86.178	1.5174	2.829	293	0.8526	−0.49 (0.5)	3.90	26	11
n-$C_{16}H_{34}$	226.448	1.3407		n-C_6H_{14}	86.178	1.6074	2.671	333	0.8341	−0.97 (0.5)	4.01	27	11
n-$C_{16}H_{34}$	226.448	1.2932		n-C_7H_{16}	100.205	1.4629	2.947	293	0.8839	−0.31 (0.5)	3.43	28	11
n-$C_{16}H_{34}$	226.448	1.3610		n-C_7H_{16}	100.205	1.5752	2.738	349	0.8640	−0.77 (0.5)	3.56	29	11
n-$C_{16}H_{34}$	226.448	1.2931		n-C_8H_{18}	114.232	1.4238	3.026	293	0.9082	−0.19 (0.5)	3.02	30	11
n-$C_{16}H_{34}$	226.448	1.4013		n-C_8H_{18}	114.232	1.5884	2.712	379	0.8822	−0.74 (0.5)	3.19	31	11
n-C_9H_{20}	128.259	1.3928	3.068	n-C_7H_{16}	100.205	1.4721	2.928	298	0.9461	−0.043 (0.5)	1.71	32	46
n-$C_{11}H_{24}$	156.313	1.3514	3.125	n-C_7H_{16}	100.205	1.4721	2.928	298	0.9180	−0.138 (0.5)	2.31	33	46
n-$C_{20}H_{42}$	282.556	1.2898		n-C_7H_{16}	100.203	1.5004	2.873	313	0.8596	−0.550 (0.5)	4.13	34	46
n-$C_{20}H_{42}$	282.556	1.3237		n-C_7H_{16}	100.203	1.5619	2.760	343	0.8475	−0.863 (0.5)	4.20	35	46
n-$C_{36}H_{74}$	506.99	1.2983		n-C_9H_{20}	128.259	1.5222	2.807	369	0.8529	−1.25 (0.5)	5.31	36	11
n-$C_{36}H_{74}$	506.99	1.3307		n-C_9H_{20}	128.259	1.5851		399	0.8395	−1.89 (0.5)	5.41	37	11
C_2H_4	28.054	1.5269	3.0114	CH_4	16.043	2.3053	2.6768	103.94	0.6623	−0.186 (0.399)	2.23	38	42
C_2H_6	30.070	1.5816	3.112	CH_4	16.043	2.3389	2.638	108	0.6762	−0.596 (0.32)	2.89	39	37
C_3H_8	44.097	1.4089	3.267	CH_4	16.043	2.3389	2.638	108	0.6024	−0.826 (0.45)	3.81	40	37
C_3H_8	44.097	1.4089	3.267	C_2H_6	30.070	1.5816	3.112	108	0.8908	−0.485 (0.296)	3.19	41	37
cyc.-C_6H_{12}	84.162	1.2546	2.917	$C(CH_3)_4$	72.151	1.6358	2.567	273	0.7669	−1.00 (0.5)	1.47	42	9
$(C_6H_5)_2$	154.212	1.0069	3.233	C_6H_6	78.114	1.2122	2.735	343	0.8307	−0.30 (0.5)	2.93	43	9
BrC_6H_5	157.010	0.6778	3.0445	C_6H_6	78.114	1.1578	2.864	308	0.5854	−0.026 (0.5)	2.28	44	49
ClC_6H_5	112.559	0.9155	2.9888	$CH_3C_6H_5$	92.141	1.1726	2.9247	308	0.7807	−0.102 (0.5)	1.27	45	49
BrC_6H_5	157.010	0.6778	3.0445	$CH_3C_6H_5$	92.141	1.1726	2.9247	308	0.5780	−0.148 (0.5)	1.79	46	49
HBr	80.912	0.4363	2.833	HCl	36.461	0.8563	2.594	195.4	0.5095	0.086 (0.473)	2.38	47	4
1,2-$Cl_2C_6H_4$	147.004	0.7690	3.1844	2,2,4-TMP^b	114.232	1.4539	2.818	298	0.5289	−0.75 (0.526)	0.906	48	23
1,3-$Cl_2C_6H_4$	147.004	0.7795	3.1327	n-C_8H_8	163.541	1.4317	3.008	298	0.5445	−0.318 (0.51)	0.88	49	23
1,3-$Cl_2C_6H_4$	147.004	0.7795	3.1327	2,2,4-TMP^b	114.232	1.4539	2.818	298	0.5362	−0.585 (0.48)	0.83	50	23
CCl_4	153.823	0.6125	2.929	$C(CH_3)_4$	72.151	1.6358	2.567	273	0.3744	−0.50 (0.5)	1.83	51	9
Aniline	93.129	0.9785	2.963	C_6H_6	78.114	1.1374	2.915	293	0.8603	−0.23 (0.54)	1.50	52	41
Kr	83.800	0.4095	2.658	CH_4	16.043	2.4085	2.5621	115.8	0.1700	−0.027 (0.396)	3.37	53	1
Ar	39.948	0.7059	2.656	N_2	28.013	1.2887	2.479	84	0.5477	−0.18 (0.5)	1.27	54	9
O_2	31.999	0.82815	2.770	N_2	28.013	1.2359	2.585	77	0.6700	−0.21 (0.5)	1.0	55	9
Xe	131.300	0.33733	2.664	Kr	83.800	0.4862	2.238	161.4	0.6938	−0.68 (0.468)	2.34	56	2
ClC_6H_5	112.559	0.9155	2.989	C_6H_6	78.114	1.1578	2.864	308	0.7907	0.01 (0.5)	1.73	57	49
CCl_4	153.823	0.6311	2.843	cyc.-C_6H_{12}	84.162	1.292	2.832	298	0.4885	0.16 (0.5)	1.69	58	9
BrC_6H_5	157.010	0.6778	3.044	ClC_6H_5	112.559	0.9155	2.989	308	0.7403	0.0039 (0.5)	1.54	59	49
CH_3I	141.939	0.4416	3.032	$CHCl_3$	119.373	0.6759	2.962	298	0.6532	0.024 (0.5)	0.874	60	24
CH_3I	141.939	0.4416	3.032	C_6H_6	78.114	1.1446	2.897	298	0.3857	0.36 (0.5)	1.286	61	24

(*Continued*)

Table 2 (*Continued*)

Solute (1)	M_w (g mol^{-1})	v_1° (cm^3 g^{-1})	V_c/V_1°	Solvent (0)	M_w (g mol^{-1})	v_0° (cm^3 g^{-1})	V_c/V_0°	T (K)	v_1°/v_0°	$\Delta V_m(x_1)_{obs.}$[a] (cm^3 mol^{-1})	n	No. (point)	Ref.
PIB	4.0×10^4	1.0906		cyc.-C_6H_{12}	84.162	1.2921	2.833	298	0.84405	−0.00141(0.5)	1.35	62	14
PIB	4.0×10^4	1.0906		n-C_5H_{12}	70.153	1.6094	2.637	298	0.6776	−0.0127 (0.54)	1.97	63	16
PIB	4.0×10^4	1.0906		n-C_6H_{14}	86.178	1.5267	2.812	298	0.7143	−0.00857(0.54)	1.80	64	16
PIB	4.0×10^4	1.0906		n-C_7H_{16}	100.205	1.4721	2.928	298	0.7408	−0.00615(0.53)	1.69	65	16
PIB	4.0×10^4	1.0906		n-$C_{10}H_{22}$	142.286	1.3769	3.094	298	0.7921	−0.0029 (0.53)	1.49	70	16
PIB	4.0×10^4	1.0906		n-$C_{16}H_{34}$	226.448	1.2992		298	0.8394	−0.0008 (0.515)	1.31	71	16
PS	5.1×10^4, 9.72×10^4	0.9336		MEK	72.107	1.2502	2.962	298	0.7468	−0.008 (0.5)	1.76	72	17
PS	5.1×10^4, 9.72×10^4	0.9336		$C_2H_5C_6H_5$	106.168	1.1592	3.0389	298	0.8054	−0.003 (0.46)	1.49	73	18
PS	5.1×10^4, 9.72×10^4	0.9336		cyc.-C_6H_{12}	84.162	1.292	2.832	298	0.7225	−0.0014 (0.5)	1.53	74	19
PDMS	10^5	1.0312		C_6H_6	78.114	1.1445	2.897	298	0.9011	−0.00077(0.39)	1.25	75	20
PDMS	10^5	1.0312		cyc.-C_6H_{12}	84.162	1.292	2.832	298	0.7980	0.00053(0.51)	1.33	76	20
C_6H_6	78.114	1.1104	2.735	$C(CH_3)_4$	72.151	1.6359	2.567	273	0.6788	−0.50 (0.5)	0.81	77	9
CCl_4	153.823	0.6312	2.843	Diethyl ether	74.123	1.4124	2.674	298	0.4469	−0.71 (0.5)	2.07	78	32
$CHCl_3$	119.378	0.6759	2.962	Diethyl ether	74.123	1.4124	2.674	298	0.4786	−0.75 (0.5)	1.45	79	32
CH_2Cl_2	84.933	0.7597	2.991	Diethyl ether	74.123	1.4124	2.674	298	0.5379	−1.34 (0.5)	0.79	a	32
C_5H_5N	79.102	1.0279	3.124	C_6H_6	78.114	1.1445	2.897	298	0.8982	−0.201 (0.5)	1.14	b	32
$CHCl_3$	119.378	0.66247	3.0220	$(C_2H_5)_3N$	101.193	1.3545	2.845	283	0.4891	−1.93 (0.5)	0.74	c	32
C_6H_6	78.114	1.1445	2.897	Acetone	58.08	1.2718	2.829	298	0.8999	−0.07 (0.5)	1.82	d	32

[a] In the case of polymer solutions $\Delta v_m/v^\circ$
[b] 2,2,4-TMP, 2,2,4-trimethyl pentane

Table 3 Excess volume of mixing Δv_m in region III

Solute (1)	M_w (g mol^{-1})	v_1° (cm^3 g^{-1})	V_c/V_1°	Solvent (0)	M_w (g mol^{-1})	v_0° (cm^3 g^{-1})	V_c/V_0°	T (K)	v_1°/v_0°	$\Delta V_m(x_1)_{obs.}$[a] (cm^3 mol^{-1})	n	No. (point)	Ref.
1,2-$Cl_2C_6H_4$	147.004	0.7690	3.1844	n-C_8H_{18}	163.541	1.4317	3.008	298	0.6345	−0.414 (0.5)	−0.20	80	23
cyc.-C_6H_{12}	84.162	1.2844	2.849	n-C_6H_{14}	86.178	1.5163	2.832	293	0.8479	0.15 (0.5)	0.60	81	9
C_6H_6	78.114	1.1445	2.897	n-C_6H_{14}	86.178	1.5267	2.812	298	0.7497	0.46 (0.5)	0.12	82	9
CH_3I	141.939	0.4416	3.032	CCl_4	153.823	0.6312	2.843	298	0.6995	0.112 (0.5)	0.20	83	24
1-ClC_4H_9	92.569	1.1573	2.912	Butan-2-ol	74.123	1.2665	2.855	313	0.9138	0.543 (0.41)	0.79	84	7
C_6H_6	78.114	1.1445	2.897	2,2,4-TMP	114.232	1.4539	2.818	298	0.7872	0.5 (0.5)	−0.65	85	22
PIB	4.0×10^4	1.0906		C_6H_6	78.114	1.1445	2.897	298	0.9529	0.0034 (0.55)	0.25	86	13
NR[b]	4.0×10^4	1.0951		C_6H_6	78.114	1.1445	2.897	298	0.9569	0.00089(0.5)	0.83	87	12
C_6H_6	78.114	1.1445	2.897	$(C_2H_5)_3N$	101.193	1.3812	2.790	298	0.8286	0.005 (0.5)	−0.03	88	2
Acetone	58.080	1.2718	2.829	n-C_6H_{14}	86.178	1.5267	2.812	298	0.8330	0.24 (0.5)	−0.56	89	32
ClC_6H_5	112.559	0.9083	3.012	n-C_8H_{18}	163.541	1.4317	3.008	298	0.6345	−0.046 (0.50)	−0.72	90	23

[a] In the case of polymer solutions $\Delta v_m/v^\circ$
[b] NR, natural rubber

Table 4 Excess volume of mixing Δv_m in region IV

Solute (1)	M_w (g mol^{-1})	v_1° (cm^3 g^{-1})	V_c/V_1°	Solvent (0)	M_w (g mol^{-1})	v_0° (cm^3 g^{-1})	V_c/V_0°	T (K)	v_1°/v_0°	$\Delta V_m(x_1)_{obs.}$[a] (cm^3 mol^{-1})	n	No. (point)	Ref.
CH_4	16.043	2.211	2.791	Ar	39.948	0.7297	2.569	91	3.030	0.18 (0.5)	0.04	100	9
O_2	31.999	0.8525	2.691	Ar	39.948	0.7059	2.656	84	1.208	0.14 (0.5)	0.94	101	9
HCl	36.461	0.8596	2.584	Xe	131.300	0.3669	2.449	195.4	2.343	0.64 (0.32)	−1.06	102	3
HBr	80.912	0.4363	2.833	Xe	131.300	0.3656	2.449	195.4	3.380	0.198 (0.33)	0.21	103	4
N_2O	44.013	0.8063	2.745	Xe	131.300	0.3538	2.540	182.3	2.279	0.669 (0.39)	−0.65	104	6
n-C_6H_{14}	86.178	1.5483	2.773	n-C_6F_{14}	338.044	0.60933	2.146	308	2.541	5.38 (0.5)	−1.1	105	9
cyc.-$CH_3C_6H_{11}$	98.189	1.3707	2.734	cyc.-$CF_3C_6F_{11}$	350.055	0.5976		338	2.294	7.30 (0.5)	−0.78	106	9
C_6H_6	78.114	1.1445	2.897	CCl_4	153.823	0.6311	2.843	298	1.814	0.01 (0.5)	−0.10	107	9
cyc.-C_8H_{16}	112.216	1.2018		1,2-$Cl_2C_6H_4$	147.004	0.7690	3.184	298	1.5628	0.469 (0.47)	0.964	108	23
cyc.-C_8H_{16}	112.216	1.2018		1,3-$Cl_2C_6H_4$	147.004	0.7795	3.132	298	1.5417	0.568 (0.52)	0.966	109	23
$CHCl_3$	119.378	0.6759	2.962	CCl_4	153.823	0.6312	2.843	298	1.0708	0.166 (0.5)	0.62	110	24
CH_2Cl_2	84.933	0.7597	2.9912	CCl_4	153.823	0.6312	2.843	298	1.2036	0.319 (0.5)	−0.196	111	24
C_6H_6	78.114	1.1448	2.897	*p*-Dioxane	88.107	0.9728	2.777	298	1.1765	−0.074 (0.25)	0.79	112	38
PDMS	10^5	1.0312		ClC_6H_5	112.559	0.9415	2.906	298	1.0952	−0.0051(0.63)	0.20	113	20
o-Xylene	106.168	1.1416	3.0446	CCl_4	153.823	0.6312	2.843	298	1.8085	−0.0045(0.50)	0.78	114	32
C_5H_5N	79.102	1.0433	3.0777	$CHCl_3$	119.378	0.6864	2.917	308	1.5201	−0.132 (0.5)	0.37	115	32
MEK	72.107	1.2509	2.9602	C_6H_6	78.114	1.1445	2.897	298	1.0929	−0.116 (0.5)	0.72	116	32
$CH_3C_6H_5$	92.141	1.1534	2.973	Aniline	93.129	0.97847	2.963	293	1.1788	−0.107 (0.468)	1.13	117	41
$CHCl_3$	119.378	0.6819	2.936	CCl_4	153.823	0.6365	2.819	303	1.0415	0.615 (0.5)	0.68	118	49

[a] In the case of polymer solutions $\Delta v_m/v^\circ$

DISCUSSION

It is of interest to refer to theoretical studies on Δv_m. An accurate and useful expression for Δv_m in simple liquid mixtures, known as the Redlich–Kister equation, is given by:

$$\Delta v_m = x_0 x_1 [A_0 + A_1(1 - 2x_0) + A_2(1 - 2x_0)^2] \quad (22)$$

where A_i is a constant determined experimentally. On the other hand, Δv_m in this study is given by equation (16) with equation (19) for $Y(x_0)$ and there is only one adjustable parameter n, which is obtained by the best fit with the data. It is found that it is very difficult to predict Δv_m for a wide concentration range from equations (13) and (16) with equation (19) because a small error in concentration ($\Delta x_0/x_0 = 10^{-3}$–10^{-4}) cause large errors in Δv_m of the order of $\Delta v_m/v_m \sim 10^{-3}$. In other words, data with very high accuracy are needed for the concentration and the specific volume of the mixture in predicting Δv_m as a function of concentration.

It was also found in this study that there is a strong correlation between the sign of Δv_m and v_1°/v_0° with mixtures with $v_1^\circ/v_0^\circ > 1$ giving $\Delta v_m > 0$ and with $v_1^\circ/v_0^\circ < 1.0$ giving $\Delta v_m < 0$ except for polymer solutions with $\Delta v_m > 0$. Although we cannot explain this behaviour theoretically, it is reasonable to say that a geometrical packing of the molecules in the pure state has a dominant effect on the packing of different molecules in a mixture and on the excess volume of mixing.

A useful expression for Δv_m and other excess functions such as Δh_m and Δg_m have been derived by Rigby *et al.*[35], Mansoori *et al.*[36] and Flory *et al.* Good predictions are obtained by Flory *et al.* for Δv_m for simple liquid mixtures and polymer solutions[9–20] where the excess volume is related to not only the volume of the pure components but also to the thermal expansion and thermal pressure coefficients in the pure state and an adjustable parameter X_{12}. It is emphasized here that the specific volumes of pure components and the parameter n are sufficient to predict the excess volume Δv_m and the procedure used for deriving Δv_m can be applied to derive Δh_m and Δg_m for a mixture.

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