Thermochimica Acta, 160 (1990) 253–266
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

APPLICATION OF THE FLORY AND SANCHEZ–LACOMBE THEORIES TO THE EXCESS ENTHALPY AND EXCESS VOLUME OF ETHER + HYDROCARBON SYSTEMS

TERESA TRESZCZANOWICZ

Institute of Physical Chemistry, Polish Academy of Sciences, 44/52 Kasprzaka Str.,
01-224 Warsaw (Poland)

(Received 19 September 1989)

ABSTRACT

Excess volume measurements for 2,5-dioxahexane + heptane and + octane, for 3,5-dioxaheptane + heptane and for isopropyl ether + heptane at 298.15 K are reported. The changes in excess volume observed in this work and described in the literature, as well as the reported excess enthalpy data for chain aliphatic ether + alkane systems as a function of composition are discussed in terms of the new Flory and the Sanchez–Lacombe theories. The interaction parameters for this class of mixtures have been correlated with the oxygen-atom surface fraction in the ether molecule.

INTRODUCTION

The excess volume in chain ether + alkane systems has not been sufficiently investigated except for some preliminary studies using the Flory theory [1]. Therefore, no attempt has been made to describe this whole class of mixtures, including their excess enthalpies. An excellent experimental study of V^E and H^E in a series of acetal + alkane systems has been presented by Meyer et al. [2]. The excess properties of several ether + alkane binary systems have also been investigated, namely, di-*n*-butyl ether + hexane [3], di-*n*-propyl ether + heptane, 2,5,8-trioxanonane + heptane [4,5] and 3,6-dioxaoctane + heptane [6]; and the excess enthalpy of linear ethers or acetals + heptane or + cyclohexane mixtures have been investigated [7].

The thermodynamic properties such as excess Gibbs free energy G^E and excess enthalpy H^E of linear mono- or polyethers + *n*-alkanes have been extensively investigated in terms of the group contribution model in the random-mixing approximation [8–10]. However, lattice theories describe neither the pure liquid properties nor the change of volume upon mixing; the equation of state principally predicts a change of volume upon mixing.

Consequently, the purpose of this paper is to demonstrate the possibility of predicting the excess enthalpy and excess volume of aliphatic ether +

alkane systems in terms of equation-of-state theories such as the new Flory theory and the Sanchez–Lacombe theory, using one set of adjustable interaction parameters χ_{12} for a given model.

The systems formed by 2,5-dioxahexane (DOHX) + heptane and + octane, by 3,5-dioxaheptane (DOHP) + heptane and by isopropyl ether (IPE) + heptane at 298.15 K are studied, together with the available literature data on excess volume [11] and excess enthalpy [12,13].

EXPERIMENTAL

The hydrocarbons were purified by conventional methods to give materials 99.9% pure, by GLC testing. 2,5-Dioxahexane (Koch-Light pure grade) was purified as previously described [14]. Isopropyl ether (Aldrich, 99%) was twice-distilled over sodium through a distillation column packed with glass helixes. The purity of the materials was determined by GLC and their properties are given in Table 1.

The excess volumes V^E were obtained by measuring the liquid-mixture densities with an oscillator-type densimeter (Anton Paar, DMA 02C). The operating procedure was described previously [19]. Samples of mixtures of known concentration, capacity about 10 ml, were prepared synthetically in a small glass vessel equipped with a silicone rubber diaphragm and with the vapour space reduced to a minimum to avoid evaporation effects. Water, *n*-heptane and air were used as standards to calibrate the densimeter. The temperature of the oscillator chamber, 298.15 K, was controlled to within ± 0.01 K by using a quartz HP thermometer. The benzene + cyclohexane system was adopted as a standard for testing the densimeter. For excess volume V^E of the benzene–cyclohexane system, the coefficients of the fitting equation (eqn. (1)) are given in Table 2. Our results differ by no more than ± 0.006 cm^3 mol^{-1} from those of Kiyohara and Benson [19] and Takenaka et al. [20], which were obtained by the same technique. The densities of the pure components agreed with the literature values to better than 5×10^{-5} g cm^{-3}.

RESULTS

The experimental V^E data for 2,5-dioxahexane + heptane and + octane, for 3,5-dioxaheptane + heptane, and for isopropyl ether + heptane at 298.15 K were fitted with the Redlich–Kister smoothing equation

$$V^E\ (\mathrm{cm^3\ mol^{-1}}) = x_1 x_2 \sum_{i=1}^{m} c_i (x_1 - x_2)^{i-1} \qquad (1)$$

The coefficients c_i, determined by the least-squares method with all the data

TABLE 1

Physical constants of pure components of the investigated systems and data used in calculation of the equation-of-state parameters at 298.15 K[a]

Component	n_D		ρ (g cm^{-3})		$10^3\alpha_P$ (K^{-1})	C_p (J K^{-1} mol^{-1})	u (m s^{-1})	$10^6 K_T$ (atm)
	experimental value	literature value	experimental value	literature value				
Ethers								
Methyl butyl (MBE)	1.3718	1.3712 [15]	0.7394	0.7393 [15]	1.3437	192.79	1078.77	151.47
n-Propyl (NPE)				0.7419 [15]	1.3004	221.22	1086.54 [1]	147.55
Isopropyl (IPE)	1.3659	1.3655 [15]	0.7189	0.7182 [15]	1.4353	216.78	999.16	181.70
n-Butyl (NBE)				0.7641 [15]	1.1255	195.2		122.34
2,4-Dioxapentane (DOP)	1.3516	1.3509 [16]	0.8599	0.8538 [16]	1.495	162.04	1064.66	148.46
3,5-Dioxaheptane (DOHP)	1.3717	1.3710 [17]	0.8241	0.8248 [17]	1.281	188.88	1067.22	141.13
2,5-Dioxahexane (DOHX)	1.3784	1.3781 [16]	0.8616	0.8621 [16]	1.2674	191.22	1166.54	112.93
2,5,8-Trioxanonane (TON)				0.9440 [16]	1.0602	278.51	1279.68 [4]	83.25
2,5,8,11-Tetraoxadodecane (TOD)			0.9811		0.9771	366.58	1341.79	71.65
Alkane								
n-Hexane (C6)	1.3724	1.3723 [15]	0.6548	0.6548 [15]	1.387 [18]			172.65 [18]
n-Heptane (C7)	1.3852	1.3851 [15]	0.6796	0.6795 [15]	1.256 [18]			148.00 [18]
n-Octane (C8)	1.3951	1.3950 [16]	0.6984	0.6985 [15]	1.164 [18]			131.97 [18]
n-Decane (C10)				0.7263 [15]	1.051 [18]			112.43 [18]
n-Dodecane (C12)	1.4194	1.4195 [15]	0.7450	0.7452 [15]	0.96			98.0

[a] Values of α_P, C_p, u for ethers were measured by D'Arcy and Halpin [32].

TABLE 2

Coefficients c_i for the least-squares representations of V^E (cm^3 mol^{-1}) by eqn. (1) at 298.15 K

System	c_o	c_1	c_2	$\delta(V^E)$
$C_6H_6 + c-C_6H_{12}$	2.61816	−0.11162		0.0047
2,5-DOHX + C_7	4.58011	−0.05512	0.07541	0.0053
2,5-DOHX + C_8	4.86123	0.00734	0.05447	0.0055
IPE + C_7	0.95603	0.02251		0.0041
3,5-DOHP + C_7	2.79598	−0.01780		0.0069

points weighted equally, are given in Table 2 together with the standard deviations. The experimental excess volumes in the investigated systems are presented in Fig. 5 (see later) together with the reported and predicted V^E data.

The excess volume V^E observed in this work and described in the literature, as well as the reported excess enthalpy data for ether + alkane systems, are discussed below in terms of the new Flory and the Sanchez–Lacombe theories. The single parameters of interactions, χ_{12} and ϵ_{12}, were calculated from the smoothed experimental V^E and H^E values at equimolar concentration.

THE FLORY THEORY

According to the free-volume Flory theory, the equation of state at $p = 0$, V^E and H^E are given by the following relations

$$\tilde{T} = (1 - \tilde{\rho}^{1/3})\tilde{\rho} \tag{2}$$

$$V^E = V^\star\left[\tilde{V} - \left(\phi_1\tilde{\rho}_1^{-1} + \phi_2\tilde{\rho}_2^{-1}\right)\right] \tag{3}$$

$$H^E = \chi_{12}x_1V_1^\star(1-\theta_1)\tilde{\rho} - P_1^\star V_1^{\star\prime}(\tilde{\rho}-\tilde{\rho}_1)x_1 - P_2^\star V_2^\star(\tilde{\rho}-\tilde{\rho}_2)x_2 \tag{4}$$

where $\tilde{\rho} = 1/\tilde{v}$. The notation closely follows that of Orwoll and Flory [21]. The pure-state characteristic parameters, characteristic volume $V_i^\star$, pressure $P_i^\star$ and temperature $T_i^\star$, are given in Table 3. These parameters were calculated by the method proposed by Flory [22] and by Benson et al. [23] using the data on molar volume V_i, isobaric thermal expansivity ($\alpha_{P,i}$) and isothermal compressibility $K_{T,i}$ given in Table 1.

The isothermal compressibility coefficient K_T, was calculated from the ultrasound speed u, the thermal expansion and the isobaric heat capacity $C_p^\ominus$ using the formula

$$K_{T,i} = K_{S,i} + TV_i\alpha_{P,i}^2/C_{p,i}^\ominus \tag{5}$$

where $K_{S,i} = (\rho_i u_i^2)^{-1}$, the isentropic compressibility coefficient.

TABLE 3

Characteristic parameters of pure components for the Flory and Sanchez–Lacombe theories at 298.15 K

Component	Flory			Sanchez–Lacombe		
	$V^\star$ (cm^3 mol^{-1})	$P^\star$ (kPa)	$T^\star$ (K)	$V^\star$ (cm^3 mol^{-1})	$P^\star$ (MPa)	$T^\star$ (K)
Ether						
Methyl butyl (MBE)	90.7	462.8	4501	102.6	361.7	484.6
n-Propyl (NPE)	105.5	454.3	4571	118.9	357.2	483.4
Isopropyl (IPE)	106.7	422.5	4368	120.6	330.3	466.3
n-Butyl (NBE)	133.9	450.3	4911	150.0	359.0	503.6
2,4-Dioxapentane (DOP)	66.3	574.2	4291	75.3	444.8	469.4
3,5-Dioxaheptane (DOHP)	97.0	465.3	4604	109.5	365.5	490.1
2,5-Dioxahexane (DOHX)	80.4	573.0	4628	90.7	450.6	491.2
2,5,8-Trioxanonane (TON)	113.3	610.7	5068	126.5	489.9	511.6
2,5,8,11-Tetraoxadodecane (TOD)	146.2	636.4	5299	162.4	515.4	521.0
Alkane						
n-Hexane (C6)	99.5	424.2	4436	112.7	331.1	477.5
n-Heptane (C7)	113.6	431.9	4648	127.9	340.5	489.5
n-Octane (C8)	127.7	436.8	4827	143.3	347.0	499.7
n-Decane (C10)	155.8	447.0	5091	173.8	358.8	513.4
n-Dodecane (C12)	184.4	454.6	5351	205.0	368.1	528.4

The Sanchez–Lacombe theory

The equation of state and the relations for excess volume and excess enthalpy are given as follows

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\left(1 - \frac{1}{r}\right)\tilde{\rho} + \ln(1 - \tilde{\rho})\right] = 0 \qquad (6)$$

$$H^{\mathrm{E}} = RTr\left[\chi_{12}\tilde{\rho}\phi_1\phi_2 - \left(\tilde{\rho}\phi_1 - \tilde{\rho}_1\phi_1^{\ominus}\right)T_1^{-2} - \left(\tilde{\rho}\phi_2 - \tilde{\rho}_2\phi_2^{\ominus}\right)T_2^{-2}\right] \qquad (7)$$

where $\chi_{12} = \epsilon_{12} = \Delta\epsilon_{12}^\star/RT$ and $\Delta\epsilon_{12}^\star = \epsilon_{11}^\star + \epsilon_{22}^\star - 2\epsilon_{12}^\star$, and $\tilde{\rho} = 1/\tilde{v}$. The notation closely follows that of Sanchez and Lacombe [24]. The pure-state characteristic parameters $V_i^\star$, $P_i^\star$ and $T_i^\star$ are given in Table 3 and were estimated from the molar volumes coefficients of thermal expansion, ultrasound speed and isobaric heat capacity, as given in Table 1.

The relation for excess volume is the same as for the Flory theory and is given by eqn. (3).

CORRELATION OF THE INTERACTION PARAMETERS

The correlation method for the interaction parmeters with molecular structure is based on the molecular surface interactions of groups (MSIG) as proposed by Kehiaian et al. [8,9], Redlich et al. [25] and Manzini and Crescenzi [26]. In each theory the interaction parameters were correlated with the surface fraction of oxygen, $\alpha_o^{(1)}$, in the ether molecule.

Three kinds of contact surfaces are distinguishable: oxygenic, with the surface fraction $\alpha_o^{(1)} = n_o^{(1)} s_o^\star / s_1^\star$; aliphatic corresponding to the CH_3 and CH_2 groups on the ether molecule (1), with the surface fraction defined as $\alpha_e^{(1)} = 1 - \alpha_o^{(1)}$; and that on the alkane molecule (2), with $\alpha_a^{(2)} = 1$.

The molecular surface $s_1^\star$ (10^9 cm^2 mol^{-1}) $= 4.24 + 0.6 n_o^{(1)} + 1.35(n_c^{(1)} - 2)$ for the ether molecule (1), and $s_o^\star = 0.6 \times 10^9$ cm^2 mol^{-1} for the oxygen atom contribution were taken from van der Waals surfaces [27], where $n_o^{(1)}$ and $n_c^{(1)}$ are the number of oxygen and carbon atoms respectively.

Therefore, three contact interaction interchange parameters can be distinguished: $\chi_{o,e}^\star$ between oxygen and ether aliphatic groups; $\chi_{o,a}^\star$ between oxygen and alkane aliphatic groups; and $\chi_{e,a}^\star$ between aliphatic groups of the ether and alkane.

To reduce the number of fitting parameters, the following interrelation is assumed

$$\chi_{o,e}^\star = \chi_{o,a}^\star + \chi_{e,a}^\star \tag{8}$$

By using a general relation between the interchange surface parameters and the integral interaction parameter χ_{12} given elsewhere, [10,28] the following simple relation is obtained

$$\chi_{12} = \left(\alpha_o^{(1)}\right)^2 \chi_{o,a}^\star + \chi_{e,a}^\star \qquad (\chi_{12} = \epsilon_{12}) \tag{9}$$

where χ_{12} are the Flory and ϵ_{12} the Sanchez–Lacombe integral interaction parameters.

RESULTS AND DISCUSSION

The integral interaction parameters χ_{12} for both theories are calculated from equimolar values of the experimental excess enthalpy $H_{0.5}^E$ and excess volume $V_{0.5}^E$ data.

The results of the calculations are summarised in Tables 4 and 5, and are illustrated in Figs. 1–4 for the two investigated theories, and compared with the values correlated by eqn. (9).

The interchange parameters $\chi_{o,a}^\star$ and $\chi_{e,a}^\star$ of eqn. (9) were determined by a linear regression method from the experimental integral interaction parameters χ_{12} and are summarised in Table 6. From Figs. 1–4, it appears that the correlation equation, eqn. (9), gives a good fit to the experimental χ_{12} values, except for acetal (DOP, DOHP) + alkane systems affected by the effect of the proximity of oxygen atoms in the ether molecule, which leads to decreased V^E and H^E values as compared with the systems formed by ethers having the same number of oxygen atoms but more separated. Tables

TABLE 4

Comparison of the experimental results for excess enthalpy at 298.15 K with values calculated from the Flory and Sanchez–Lacombe theories

System [a]	Flory				Sanchez–Lacombe		
	$H_{0.5}^{E,\text{exp.}}$ (J mol^{-1})	$\chi_{12}^{\text{exp.}}$ (J cm^{-3})	$\chi_{12}^{\text{pred.}}$ (J cm^{-3})	$H_{0.5}^{E,\text{pred.}}$ (J mol^{-1})	$\chi_{12}^{\text{exp.}}$ (J)	$\chi_{12}^{\text{pred.}}$ (J)	$H_{0.5}^{E,\text{pred.}}$ (J mol^{-1})
2,5-DOHX + C7 [2]	1290	54.19	50.84	1210	424.0	385.3	1173
2,5,8-TON + C7 [8]	1635	55.59	57.93	1720	383.2	436.9	1837
2,5,8-TON + C10 [8]	1875	57.22	57.93	1898	455.3	436.9	1798
NPE + C7 [1]	204	7.14	7.90	226	67.5	73.0	222
IPE + C7 [29]	243	8.58	7.93	225	82.7	73.3	214
NBE + C6 [3]	93	3.31	4.89	143	28.2	51.1	168
MBE + C7 [8]	300	11.92	10.53	272	107.9	92.2	262
2,4-DOP + C7 [2] [b]	1008	48.70	73.13	1520	427.6	549.4	1341
3,5-DOHP + C6 [2] [b]	575	22.12	37.36	974	191.8	288.1	855
3,5-DOHP + C7 [2] [b]	604	22.31	37.36	1013	197.7	288.1	881

[a] Literature reference indicated in square brackets.

[b] Not taken into consideration in calculations.

4 and 5 provide a comparison of the experimental and predicted values of excess enthalpy and excess volume at equimolar concentration. Figures 5 and 6 illustrate the prediction of the excess volume values over the whole concentration range for some mono-and polyether systems. It is interesting

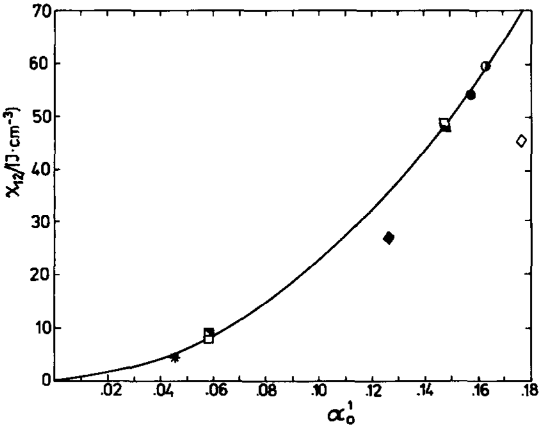

Fig. 1. Integral interaction parameter values χ_{12} in the Flory theory calculated from experimental V^E data at 298.15 K vs. oxygen fraction of ether molecule $\alpha_0^{(1)}$ for the systems: ◑, 2,5,8,11-tetraoxadodecane + n-dodecane; ●, 2,5,8-trioxanonane + n-heptane; ⬒, 2,5-dioxahexane + n-octane; ◣, 2,5-dioxahexane + n-heptane; ◇, 2,4-dioxapentane + n-heptane; ◆, 3,5-dioxaheptane + n-heptane; ◩, isopropyl ether + n-heptane; □, n-propyl ether + n-heptane; and *, n-butyl ether + n-hexane. The solid line is calculated from the correlation equation eqn. (9), using the values of parameters from Table 6.

TABLE 5

Comparison of the experimental results for excess volume at 298.15 K with values calculated from the Flory and Sanchez–Lacombe theories

System [a]	Flory				Sanchez–Lacombe		
	$V_{0.5}^{E,\text{ exp.}}$ (cm^3 mol^{-1})	$\chi_{12}^{\text{exp.}}$ (J cm^{-3})	$\chi_{12}^{\text{pred.}}$ (J cm^{-3})	$V_{0.5}^{E,\text{ pred.}}$ (cm^3 mol^{-1})	$\chi_{12}^{\text{exp.}}$ (J)	$\chi_{12}^{\text{pred.}}$ (J)	$V_{0.5}^{E,\text{ pred.}}$ (cm^3 mol^{-1})
2,5-DOHX + C7 (this work)	1.145	48.64	48.32	1.137	382.4	399.7	1.198
2,5-DOHX + C8 (this work)	1.215	47.88	48.32	1.226	412.3	399.7	1.177
2,5,8-TON + C7 [4]	0.902	54.16	54.99	0.923	342.4	453.8	1.165
2,5,8,11-TOD + C12 [30]	1.690	59.68	58.86	1.666	488.1	485.2	1.679
NPE + C7 [6]	0.252	7.99	7.98	0.252	75.9	72.3	0.240
IPE + C7 [29]	0.241	9.03	8.01	0.207	86.4	72.5	0.190
NBE + C6 [3]	−0.044	4.27	5.15	−0.015	33.7	49.3	0.007
2,4-DOP + C7 [2] [b]	1.217	45.54	69.27	1.775	427.9	569.7	0.977
3,5-DOHP + C7 [2] [b]	0.791	27.19	35.66	1.643	241.9	296.9	1.656

[a] Literature reference indicated in square brackets.

[b] Not taken into consideration in calculations.

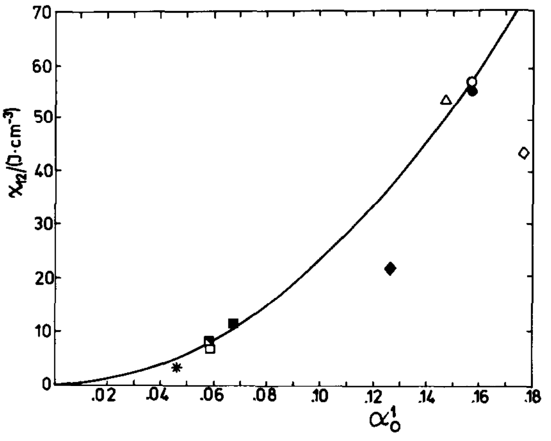

Fig. 2. Integral interaction parameter values χ_{12} in the Flory theory calculated from experimental H^E data at 298.15 K vs. oxygen fraction of ether molecule $\alpha_o^{(1)}$ for the systems: ○, 2,5,8,-trioxanonane + *n*-decane; ●, 2,5,8-trioxanonane + *n*-heptane; △, 2,5-dioxahexane + *n*-heptane; ◇, 2,4-dioxapentane + *n*-heptane; ◆, 3,5-dioxaheptane + *n*-heptane; ■, butyl methyl ether + *n*-heptane; ◩, isopropyl ether + *n*-heptane; □, *n*-propyl ether + heptane; and *, *n*-butyl ether + *n*-heptane. The solid line is calculated from the correlation equation eqn. (9), using the values of parameters from Table 6.

to note that for the di-*n*-butyl ether + *n*-hexane system, slight positive–negative values are predicted by the Flory theory.

Lattice theories predict values of the excess enthalpy with the same

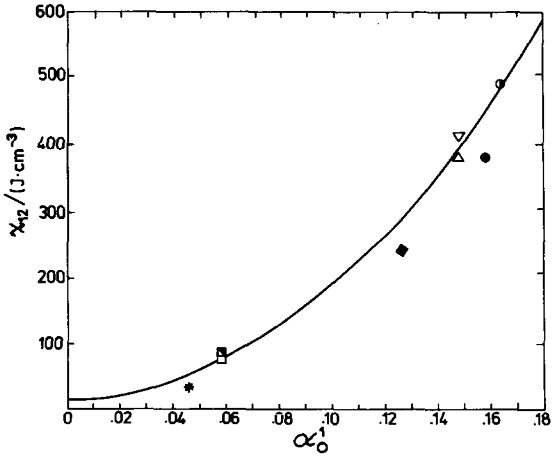

Fig. 3. Integral interaction parameter values, χ_{12} in the Sanchez–Lacombe theory calculated from experimental V^E data at 298.15 K vs. oxygen fraction of ether molecule $\alpha_o^{(1)}$ for the systems: ◑, 2,5,8,11-tetraoxadodecane + *n*-dodecane; ▽, 2,5-dioxahexane + *n*-octane; △, 2,5-dioxahexane + *n*-heptane; ●, 2,5,8-trioxanonane + *n*-heptane; ◇, 3,5-dioxaheptane + *n*-heptane; ◩, isopropyl ether + *n*-heptane; □, *n*-propyl ether + *n*-heptane; and *, *n*-butyl ether + *n*-hexane, The solid line is calculated from the correlation equation eqn. (9), using the values of parameters from Table 6.

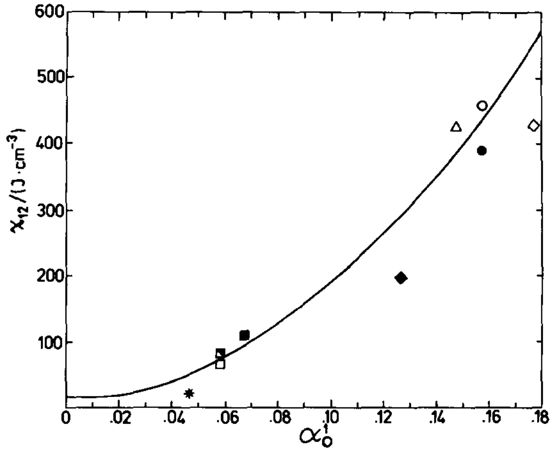

Fig. 4. Integral interaction parameter values χ_{12} in the Sanchez–Lacombe theory calculated from experimental H^E data at 298.15 K vs. oxygen fraction of ether molecule $\alpha_o^{(1)}$ for the systems: ○, 2,5,8-trioxanonane + *n*-decane; ◇, 2,4-dioxapentane + *n*-heptane; △, 2,5-dioxahexane + *n*-heptane; ●, 2,5,8-trioxanonane + *n*-heptane; ◆, 3,5-dioxaheptane + *n*-heptane; ■, butyl methyl ether + *n*-heptane; ◩, isopropyl ether + *n*-heptane; □, *n*-propyl ether + *n*-heptane; and *, *n*-butyl ether + *n*-hexane. The solid line is calculated from the correlation equation eqn. (9), using the values of parameters from Table 6.

overall accuracy [9] except that, in contrast with the Flory theory, they do not yield excess volume.

In conclusion, we can say that the Flory free-volume theory describes the excess volume much better than does the Sanchez–Lacombe theory. However, the Sanchez–Lacombe theory gives better results for prediction of the excess enthalpy. In general, both these theories can be regarded as qualitatively equivalent (Table 6).

The same conclusion was reached by Kimura and Murakami [31], who applied these theories to predict excess enthalpy and excess volume for

TABLE 6

The interchange parameters, $\chi_{s,t}^{\star}$, of eqn. (9) determined by linear regression from the experimental integral interaction parameters, χ_{12} and ϵ_{12}, of the Flory and Sanchez–Lacombe theories, the correlation coefficient c_c for χ_{12}, ϵ_{12} representation and the mean deviation of the excess property $X^E = H^E$, V^E

Theory	Property	$\chi_{o,a}^{\star}$	$\chi_{e,a}^{\star}$	c_c	δX^{E} [a]
F	$H_{0.5}^E$ J mol^{-1})	2.20449	0.0004	0.9972	51
F	$V_{0.5}^E$ (cm^3 mol^{-1})	2.34628	−0.0002	0.9995	0.0216
S-L	$H_{0.5}^E$ (J mol^{-1})	16.2349	0.021	0.9842	38
S-L	$V_{0.5}^E$ (cm^3 mol^{-1})	16.41474	0.017	0.9763	0.1260

[a] Mean deviation $\delta(X^E) = (\Sigma_i(X^{E,\mathrm{exp.}} - X^{E,\mathrm{pred.}})^2/n)^{1/2}$ where n is the number of experimental data points.

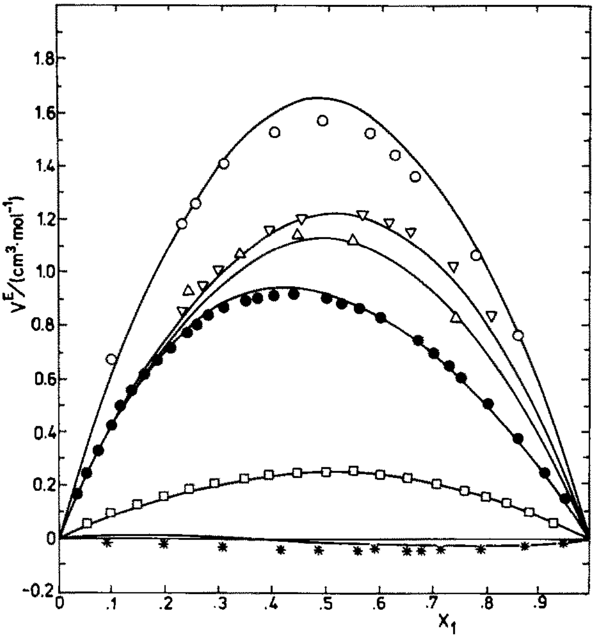

Fig. 5. The excess molar volume V^E for ether + alkane mixtures at 298.15 K vs. the mole fraction of ether for the systems: ○, 2,5,8,11-tetraoxadodecane + *n*-dodecane; ▽, 2,5-dioxahexane + *n*-octane; △, 2,5-dioxahexane + *n*-heptane; ●, 2,5,8-trioxanonane + *n*-heptane (4); □, di-*n*-propyl ether + *n*-heptane (1); and *, *n*-butyl ether + *n*-hexane (3). The solid curves are calculated from eqn. (3).

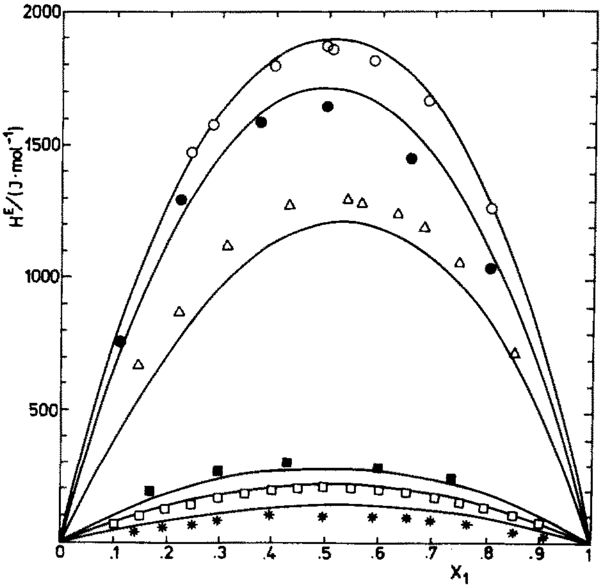

Fig. 6. The excess molar enthalpy H^E for ether + alkane mixtures at 298.15 K vs. the mole fraction of ether for the systems: ○, 2,5,8-trioxanonane + *n*-decane (8); ●, 2,5,8-trioxanonane + *n*-heptane (8); △, 2,5-dioxahexane + *n*-heptane; ■, butyl methyl ether + *n*-heptane; □, di-*n*-propyl ether + *n*-heptane (5); and *, *n*-butyl ether + *n*-hexane (3). The solid curves are calculated from eqn. (4).

fluorobenzene + aromatic hydrocarbon mixtures. It is interesting to note that one set of interchange parameters describes both excess properties with only a little less precision (cf. Table 6) for the Flory as well as the Sanchez–Lacombe theories. As already indicated, one set of interchange parameters describes the excess properties using both theories for mono- as well as polyether systems. This is in contrast with the excess Gibbs energy, where slightly lower values are observed for monoethers compared with those predicted from the lattice theory [10,28].

ACKNOWLEDGEMENT

This work has been performed under Research Project CPBR 3.20.

LIST OF SYMBOLS

α_o	oxygen surface fraction in ether molecule
α_P	isobaric thermal expansivity
c	coefficient of the Redlich–Kister equation
u	ultrasound speed
C_p	molar isobaric heat capacity
K_T	isothermal compressibility coefficient
K_s	isentropic compressibility coefficient
V	molar volume
ρ	density
χ_{12}	integral interaction parameter in Flory theory
$\chi^{\star}_{s,t}$	interchange interaction parameter in Flory theory
r	number of segments
R	gas constant
n_c	number of carbon atoms
n_o	number of oxygen atoms
H	molar enthalpy
P	pressure
T	thermodynamic temperature
ϕ	segment fraction
s_o	van der Waals surfaces for oxygen
s	van der Waals surfaces for molecule
x	mole fraction
δ	standard deviation
ϵ_{12}	interaction parameter in the Sanchez–Lacombe theory
$\Delta\epsilon_{12}$	interchange parameter in the Sanchez–Lacombe theory
M	number of coefficients in eqn. (1)

Superscripts

$\ominus$	pure component value
$\sim$	reduced value
★	characteristic value
E	excess value

Subscripts

i	component i (1 for ether, 2 for alkane)
o	oxygen atom
e	ether aliphatic group
c	alkane aliphatic group

REFERENCES

1 F. Kimura, A.J. Treszczanowicz, C.J. Halpin and G.C. Benson, J. Chem. Thermodyn., 15 (1983) 503.
2 J.R. Meyer, J.V. Metzger, K. Kehiaian and H.V. Kehiaian, Thermochim. Acta, 38 (1980) 197.
3 K.N. Marsh, J.B. Ott and M.J. Costigan, J. Chem. Thermodyn., 12 (1980) 857.
4 A.J. Treszczanowicz, C.J. Halpin and G.C. Benson, J. Chem. Eng. Data, 27 (1982) 321.
5 F. Kimura, P.J. D'Arcy and G.C. Benson, J. Chem. Thermodyn., 15 (1983) 511.
6 M.K. Kumaran, F. Kimura, C.J. Halpin and G.C. Benson, J. Chem. Thermodyn., 16 (1984) 687.
7 B. Maronglu, S. Dermini, L. Lepori, E. Matteoli and H.V. Kehiaian, J. Chem. Eng. Data, 33 (1988) 118.
8 H.V. Kehiaian, K. Sosnkowska-Kehiaian and R. Hryniewicz, J. Chim. Phys., 68 (1971) 922.
9 H.V. Kehiaian, J.-P.E. Grolier and G.C. Benson, J. Chim. Phys., 75 (1978) 1031.
10 T. Treszczanowicz, Bull. Acad. Polon. Sci., Chim., 23 (1975) 161.
11 Y.P. Handa and G.C. Benson, Fluid Phase Equil., 3 (1979) 185.
12 J.J. Christensen, R.W. Hanks and R.M. Izatt, Handbook of Heats of Mixing, Wiley–Interscience, Wiley, New York, 1982.
13 C. Christensen, J. Gmehling, P. Rasmussen and U. Weidlich, Heats of Mixing, Data Collection Binary Multicomponent Systems, Dehema Chemistry Data Series, Frankfurt am Main, 1984.
14 T. Treszczanowicz and B.C.-Y. Lu, J. Chem. Thermodyn., 18 (1986) 213.
15 American Petroleum Institute, Research Project 44, Selected Values of Properties of Hydrocarbons and Related Compounds, Thermodynamics Research Center, Texas A and M University, College Station, TX, 1975.
16 J.A. Riddick and W.B. Bunger, in A. Weissberger (ed.), Organic Solvents. Physical Properties and Methods of Purification, Wiley – Interscience, New York, 1970.
17 M. Mansson, J. Chem. Thermodyn., 1 (1969) 141.
18 A.J. Treszczanowicz and G.C. Benson, Fluid Phase Equil., 23 (1985) 117.
19 O. Kiyohara and G.C. Benson, Can. J. Chem., 15 (1973) 2489.
20 M. Takenaka, R. Tanaka and S. Murakami, J. Chem. Thermodyn., 12 (1980) 849.
21 R.A. Orwoll and P.J. Flory, J. Am. Chem. Soc., 89 (1967) 6822.

22 P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.

23 G.C. Benson, S. Murakami, V.T. Lam and J. Singh, Can. J. Chem., 48 (1969) 211.

24 R.H. Lacombe and I.C. Sanchez, J. Phys. Chem., 80 (1976) 2568.

25 O. Redlich, E.L. Derr and G.J. Pierrotti, J. Am. Chem. Soc., 81 (1959) 2283.

26 G. Manzini and V. Crescenzi, Macromolecules, 8 (1975) 195.

27 A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968 pp. 502.

28 T. Treszczanowicz, A.J. Treszczanowicz and S. Malanowski, Bull. Acad. Polon. Sci., Chim., 27 (1979) 603.

29 M. Oba, S. Murakami and R. Fuishiro, J. Chem. Thermodyn., 9 (1977) 407.

30 G.C. Benson, M.K. Kumaran, T. Treszczanowicz, P.J. D'Arcy and C.J. Halpin, Thermochim. Acta, 95 (1985) 59.

31 F. Kimura and S. Murakami, Fluid Phase Equil., 3 (1979) 93.

32 P.Y. D'Arcy and C.Y. Halpin, personal communication.