ELSEVIER

Thermochimica Acta 271 (1996) 49–58

thermochimica
acta

Excess enthalpy H^E of binary mixtures containing alkanes, methanol and tert-amyl-methyl ether (TAME)[1]

K. Kammerer, R.N. Lichtenthaler*

Physikalisch-Chemisches Institut, Universität Heidelberg,
Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

Received 15 May 1995; accepted 13 June 1995

Abstract:

Flow-calorimetric measurements of molar excess enthalpies at 298.15 K and 313.15 K and atmospheric pressure have been performed for binary mixtures of tert-amyl-methyl ether (TAME) with n-heptane, n-octane, iso-octane and methanol. The experimental results are used to test the applicability of the extended real associated solution (ERAS) model to describe thermodynamic excess properties.

Keywords: Thermodynamics; Binary liquid mixture; Excess enthalpy; ERAS model

1. Introduction

As possible substitutes of tetraethyl-lead as a gasoline blending agent, the importance of methyl-tert-butyl ether (MTBE), ethyl-tert-butyl ether (ETBE) and tert-amyl-methyl ether (TAME) arises constantly. In order to model gasoline, the thermodynamic properties of mixtures containing these ethers are of great interest. In previous papers, experimental data of binary and ternary mixtures containing MTBE and ETBE already have been published [1,2]. Continuing these investigations, in this work experimental results of the molar excess enthalpy H^E are reported for binary mixtures containing TAME. The extended real associated solution (ERAS) model [3] developed for calculating the thermodynamic properties of mixtures containing associating components is tested for the description of H^E.

---

* Corresponding author.

[1] Presented at the 11th Ulm Conference, Freiberg, Germany, 29–31 March, 1995.

SSDI 0040-6031 (95) 02588-X

Table 1

Experimental molar excess enthalpy H^E at 298.15 K and 313.15 K

x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}
x TAME + $(1-x)$n-heptane					
298.15 K					
0.093	97.3	0.387	275.4	0.706	250.5
0.196	183.4	0.515	294.8	0.796	200.2
0.284	236.1	0.594	283.1	0.897	112.7
313.15 K					
0.093	87.7	0.387	243.0	0.706	224.6
0.196	167.5	0.515	267.8	0.796	183.4
0.284	206.0	0.594	261.8	0.897	102.7
x TAME + $(1-x)$n-octane					
298.15 K					
0.099	120.8	0.404	304.1	0.715	270.1
0.205	208.5	0.504	319.0	0.805	219.1
0.296	262.4	0.615	308.3	0.904	117.1
313.15 K					
0.099	107.4	0.404	283.4	0.715	261.6
0.205	198.6	0.504	302.8	0.805	205.6
0.296	244.3	0.615	295.8	0.904	107.2
x TAME + $(1-x)$iso-octane					
298.15 K					
0.971	87.3	0.399	255.8	0.711	230.3
0.202	154.8	0.499	269.9	0.802	184.8
0.292	213.1	0.610	260.8	0.902	115.1
313.15 K					
0.971	78.4	0.399	245.8	0.711	219.2
0.202	154.9	0.499	260.4	0.802	169.9
0.292	213.2	0.610	251.0	0.902	91.3
x methanol + $(1-x)$TAME					
298.15 K					
0.096	272.7	0.503	381.5	0.904	65.6
0.199	386.7	0.594	332.2	0.951	38.2
0.311	425.3	0.684	250.0		
0.401	414.6	0.806	144.7		
313.15 K					
0.096	283.9	0.503	408.9	0.904	74.8
0.199	407.5	0.594	349.6	0.951	33.6
0.311	453.5	0.684	262.1		
0.401	449.8	0.806	159.1		

2. Experimental

TAME was obtained from Fluka Chemika, n-heptane, n-octane, iso-octane and methanol were obtained from Merck. The purity was at least 99.5% and all substances were used without further purification.

The molar excess enthalpies were measured using a modified TRONAC 1250 calorimeter. This quasi-isothermal flow calorimeter and the operating procedure have been described elsewhere in detail [4]. The errors of H^E and the mole fraction x are estimated to be $<\pm 0.01 H^E$ and $<\pm 0.001$, respectively.

3. Results and discussion

The experimental values of H^E for the four binary mixtures at 298.15 K and 313.15 K are listed in Table 1. The dependence of H^E on the mole fraction x was fitted using the Redlich-Kister equation:

$$H_m^E = x(1-x)\sum_{i=0}^{m} A_i(2x-1)^i \tag{1}$$

Values of the parameters A_i determined by least squares analysis are listed in Table 2 together with the standard deviation σ_s of the representation. Curves calculated with Eq. (1) are plotted in Figs. 1 and 2 together with the experimental values.

The values of H^E are positive in the entire mole fraction range for all binary mixtures studied. The experimental data of {TAME + n-octane} at 298.15 K agree within a few percent with the data obtained by Zhu et al. [5]. For all other mixtures investigated no data were found in the literature.

The different absolute values and different shapes of the composition-dependence of H^E reflect the differences in molecular interactions of the components. The three {ether + alkane} mixtures show very similar behaviour, with the largest values found for {TAME + n-octane} and the smallest for {TAME + iso-octane}. This is due to the structural dif-

Table 2

Parameters A_i and standard deviation σ_s for the representation of H^E by Eq. (1)

Mixture	T/K	A_0/J mol^{-1}	A_1/J mol^{-1}	A_2/J mol^{-1}	A_3/J mol^{-1}	A_4/J mol^{-1}	σ_s
TAME +	298.15	1178.2	50.8	–	–	–	1.2
n-heptane	313.15	1076.2	48.9	–	–	–	1.8
TAME +	298.15	1280.3	65.3	150.3	–	–	2.6
n-octane	313.15	1205.1	91.3	192.2	–	–	1.2
TAME +	298.15	1068.4	31.1	–31.5	237.3	–	3.4
iso-octane	313.15	1047.3	52.9	–90.4	63.1	–	2.8
Methanol +	298.15	1523.4	–977.1	294.2	–839.0	540.1	1.8
TAME	313.15	1635.7	–1104.3	263.2	–594.2	453.7	3.1

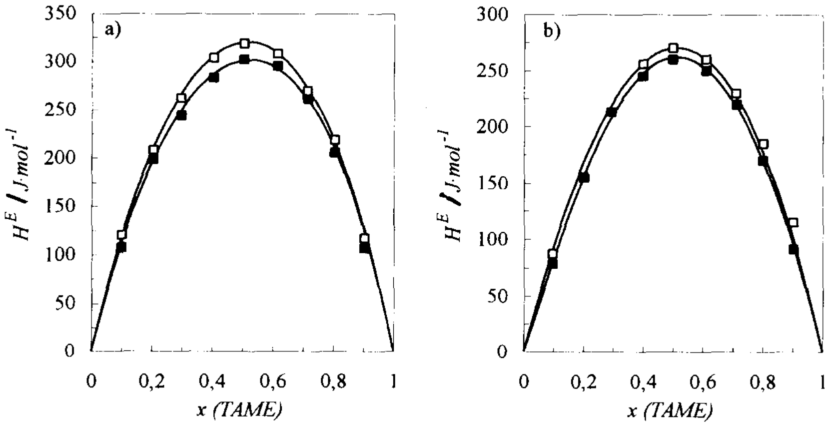

Fig. 1. Molar excess enthalpy H^E for {x TAME + $(1-x)$n-octane} (a) and {x TAME + $(1-x)$iso-octane} (b). Experimental results: □, 298.15 K, ■, 313.15 K, —, calculated with Eq. (1) using parameters of Table 2.

ferences between the chainlike n-alkanes and the quasi-globular iso-octane. For all {TAME + alkane} mixtures the maximum value of H^E decreases with increasing temperature, i.e. the molar excess heat capacity of these mixtures is negative. The maximum H^E values for the mixture {methanol + TAME} are distinctly larger than for the other binary systems. This is due to the fact that mixing causes the breaking of hydrogen bonds between the methanol molecules. Additionally the maximum is shifted towards $x(\text{methanol}) < 0.5$, which is to be expected for binary mixtures containing a self-associating component like methanol and a non-associating one. The molar excess heat capacity for {methanol + TAME} is positive, i.e. upon mixing hydrogen bonds are destroyed more effectively at higher temperature.

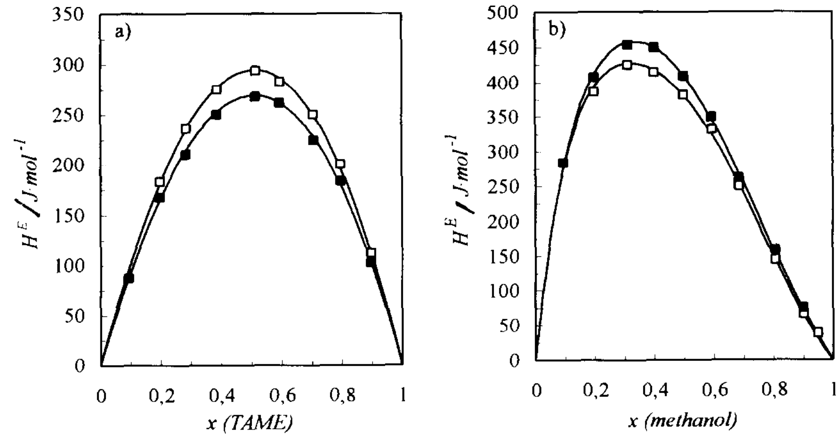

Fig. 2. Molar excess enthalpy H^E for {x TAME + $(1-x)$n-heptane} (a) and {x methanol + $(1-x)$TAME} (b). Experimental results: □, 298.15 K, ■, 313.15 K, —, calculated with Eq. (1) using parameters of Table 2.

4. Theory

The ERAS model is used to correlate the experimental results for the mixtures investigated. As this model has been described several times in detail [3,6] only a brief summary of its essential features is given here. The ERAS model is a combination of the real associated solution model [7,8] and Flory's equation of state [9,10]. The excess enthalpy of a binary mixture is expressed as the sum of a physical and a chemical contribution:

$$H^{\mathrm{E}} = H^{\mathrm{E}}_{\mathrm{phys}} + H^{\mathrm{E}}_{\mathrm{chem}} \tag{2}$$

The physical part $H^{\mathrm{E}}_{\mathrm{phys}}$ arises from van der Waals interactions, the chemical part $H^{\mathrm{E}}_{\mathrm{chem}}$ from hydrogen bonding. The expressions for the molar excess enthalpy are

$$H^{\mathrm{E}}_{\mathrm{phys}} = (x_{\mathrm{A}} V^*_{\mathrm{A}} + x_{\mathrm{B}} V^*_{\mathrm{B}}) \left(\frac{\Phi_{\mathrm{A}} P^*_{\mathrm{A}}}{\tilde{V}_{\mathrm{A}}} + \frac{\Phi_{\mathrm{B}} P^*_{\mathrm{B}}}{\tilde{V}_{\mathrm{B}}} - \frac{P^*_{\mathrm{M}}}{\tilde{V}_{\mathrm{M}}} \right) \tag{3}$$

$$\begin{aligned} H^{\mathrm{E}}_{\mathrm{chem}} &= x_{\mathrm{A}} K_{\mathrm{A}} \Delta h^*_{\mathrm{A}} (\varphi_{1\mathrm{A}} - \varphi^0_{1\mathrm{A}}) + x_{\mathrm{B}} K_{\mathrm{B}} \Delta h^*_{\mathrm{B}} (\varphi_{1\mathrm{B}} - \varphi^0_{1\mathrm{B}}) \\ &+ x_{\mathrm{A}} K_{\mathrm{AB}} \Delta h^*_{\mathrm{AB}} \frac{\varphi_{1\mathrm{B}}(1 - K_{\mathrm{A}}\varphi_{1\mathrm{A}})}{(V^*_{\mathrm{B}} / V^*_{\mathrm{A}})(1 - K_{\mathrm{B}}\varphi_{1\mathrm{B}}) + K_{\mathrm{AB}}\varphi_{1\mathrm{B}}} - \frac{P^*_{\mathrm{M}} V^{\mathrm{E}}_{\mathrm{chem}}}{\tilde{V}_{\mathrm{M}}} \end{aligned} \tag{4}$$

The physical contributions is derived from Flory's equation of state, which holds not only for the pure components (index A or B) but also for the mixture (index M):

$$\frac{\tilde{P}_i \cdot \tilde{V}_i}{\tilde{T}_i} = \frac{\tilde{V}_i^{1/3}}{\tilde{V}_i^{1/3} - 1} - \frac{1}{\tilde{V}_i \cdot \tilde{T}_i}, \quad i = \mathrm{A, B, M} \tag{5}$$

with $\tilde{P}_i = P_i / P_i^*$, $\tilde{V}_i = V_i / V_i^*$ and $\tilde{T}_i = T / T_i^*$ being the reduced pressure, volume and temperature respectively. P_i^*, V_i^* and T_i^* are the corresponding reduction parameters. x_{A} and x_{B} are the mole fractions of the components and Φ_{A} and Φ_{B} are the hard-core volume fractions defined as

$$\Phi_{\mathrm{A}} = 1 - \Phi_{\mathrm{B}} = \frac{x_{\mathrm{A}} V^*_{\mathrm{A}}}{x_{\mathrm{A}} V^*_{\mathrm{A}} + x_{\mathrm{B}} V^*_{\mathrm{B}}} \tag{6}$$

The reduction parameters of the pure components V^*_{A}, V^*_{B}, P^*_{A}, P^*_{B}, T^*_{A} and T^*_{B} are obtained by fitting Flory's equation of state to experimental PVT-data of the pure components. The reduction parameters P^*_{M} and T^*_{M} of a binary mixture are obtained using the following mixing rules:

$$P^*_{\mathrm{M}} = P^*_{\mathrm{A}} \Phi_{\mathrm{A}} + P^*_{\mathrm{B}} \Phi_{\mathrm{B}} - \Phi_{\mathrm{A}} \vartheta_{\mathrm{B}} X_{\mathrm{AB}} \tag{7}$$

$$T_{\mathrm{M}}^{*}=\frac{P_{\mathrm{M}}^{*}}{\left(P_{\mathrm{A}}\cdot\frac{\Phi_{\mathrm{A}}}{T_{\mathrm{A}}^{*}}+P_{\mathrm{B}}\cdot\frac{\Phi_{\mathrm{B}}}{T_{\mathrm{B}}^{*}}\right)} \tag{8}$$

V_{M}^{*} and also V_{M} need not be known explicitly because in order to use Eqs. (3) and (4) only $\tilde{V}_{\mathrm{M}}$ has to be known which is obtained from Eq. (5) with $\tilde{P}_{\mathrm{M}}$ and $\tilde{T}_{\mathrm{M}}$ following with the mixing rules for P_{M}^{*} and T_{M}^{*}.

The surface fraction ϑ_{B} of the substance B in the mixture is calculated in the following way:

$$\vartheta_{\mathrm{B}}=1-\vartheta_{\mathrm{A}}=\frac{(s_{\mathrm{B}}/s_{\mathrm{A}})\Phi_{\mathrm{B}}}{\Phi_{\mathrm{A}}+(s_{\mathrm{B}}/s_{\mathrm{A}})\Phi_{\mathrm{B}}} \tag{9}$$

where s_{A} and s_{B} are the surface to volume ratios of molecules A and B, which are calculated using Bondi's method of molecular group contributions [11]. X_{AB} in Eq. (7) is the energetic interaction parameter characterizing the differences of dispersive intermolecular interactions between molecules A and B in the mixture and in the pure components. X_{AB} is the only adjustable parameter of the physical part.

The chemical contribution $H_{\mathrm{chem}}^{\mathrm{E}}$ to H^{E} arises from chemical interactions between the molecules, in particular hydrogen bonding. It is assumed that there is an equilibrium of linear chain association of the components A and B and the possibility of cross-association:

$$\mathrm{A}_i+\mathrm{A}\xleftrightarrow{K_{\mathrm{A}}}\mathrm{A}_{i+1} \tag{10}$$

$$\mathrm{B}_i+\mathrm{B}\xleftrightarrow{K_{\mathrm{B}}}\mathrm{B}_{i+1} \tag{11}$$

$$\mathrm{A}_i+\mathrm{B}_j\xleftrightarrow{K_{\mathrm{AB}}}\mathrm{A}_i\mathrm{B}_j \tag{12}$$

The association constants K_i are assumed to be independent from the chain length i and their temperature dependence is given by the following equation:

$$K_i=\frac{1}{V_{1i}^{*}}\frac{c_i}{c_{i-1}c_1}=K_{i0}\exp\left\{-\frac{\Delta h_i^{*}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right\},\quad i=(\mathrm{A,B,AB}) \tag{13}$$

where V_{1j}^{*} denotes the hard-core volume of the monomeric species, Δh_i^{*} the association energy and c_i the molar concentration of the i-mer. The reaction volume Δv_i^{*} is related to the formation of the linear chain. φ_{1i} and φ_{1i}^{0} are the hard-core volume fractions of the monomeric species in the mixture and in the pure substance, respectively. These volume fractions are related to the hard-core volume fractions Φ_i and K_i. They can be determined by solving the following two non-linear equations:

Table 3

Parameters of the pure substances used in the ERAS calculations

Substance	T/K	V_{mol}/cm^3 mol^{-1}	α/ 10^{-4} K	κ_T/ 10^{-4} MPa	P^*/J cm^{-3}	V^*/cm^3 mol^{-1}	s/nm^{-1}	K_A
n-Heptane	298.15	147.42	12.48	14.47	432.2	113.7	13.97	–
	313.15	150.28	12.88	16.45	424.5	1114.2		
n-Octane	298.15	163.46	11.76	12.82	450.0	127.4	13.88	–
	313.15	166.27	12.02	14.37	413.5	129.1		
iso-Octane	298.15	166.08	11.97	15.63	378.1	129.1	14.12	–
	313.15	168.99	12.42	17.74	374.5	129.3		
TAME	298.15	133.23	12.49	13.34	466.2	102.7	14.05	–
	313.15	135.84	12.80	15.12	457.9	103.4		
Methanol[a]	298.15	40.73	11.87	12.48	422.3	32.1	16.49	986
	313.15	41.47	12.09	13.83	412.1	32.4		607

[a] $\Delta h_A^* = -25.1$ kJ mol^{-1} and $\Delta v_A^* = -5.6$ cm^3 mol^{-1} from Ref. [7].

$$\Phi_A = \frac{\varphi_{1A}}{(1-K_A \cdot \varphi_{1A})} \cdot \left(1 + \frac{V_A^{\mathrm{mol}} \cdot K_{AB}\varphi_{1B}}{V_B^{\mathrm{mol}} \cdot (1-K_B \cdot \varphi_{1B})}\right) \tag{14}$$

$$\Phi_B = \frac{\varphi_{1B}}{(1-K_B \cdot \varphi_{1B})} \cdot \left(1 + \frac{K_{AB}\varphi_{1A}}{(1-K_A \cdot \varphi_{1A})}\right) \tag{15}$$

with φ_{1A} equal to φ_{1A}^0 if $\Phi_A = 1$.

It is important to realize that for associating molecules the procedure to obtain reduction parameters of the physical contribution is somewhat different from the original one of Flory as discussed by Heintz [3]. For low pressures, i.e. $\tilde{P}_i \approx 0$, Flory's equation can be simplified. The hard-core volumes V_i^* can be calculated by introducing the thermal expansion coefficient $\alpha_i = (\partial \ln V_i / \partial T)_P$ for pure liquids by iteratively solving the following equations:

$$V_i^* = V_i \left(\frac{1 + (\alpha_i - \alpha_i^*)T}{1 + 4/3(\alpha_i - \alpha_i^*)T} \right)^3, \quad i = (\mathrm{A}, \mathrm{B}) \tag{16}$$

with

$$\alpha_i^* = \Delta v_i^* \Delta h_i^* \frac{(4K_i + 1)^{1/2} - 2K_i(4K_i + 1)^{1/2} - 1}{2K_i V_{1i}^* RT^2} \tag{17}$$

and

$$V_{1i}^* = V_i^* - K_i \Delta v_i^* \varphi_{1i} \tag{18}$$

Table 4

Parameters for the binary mixtures used in ERAS calculations

Mixture	T/K	Δh^*_{AB}/kJ mol^{-1}	Δv^*_{AB}/cm^3 mol^{-1}	X_{AB}/J cm^{-3}	K_{AB}
TAME + n-heptane	298.15	–	–	10.7	–
	313.15			9.5	
TAME + n-octane	298.15	–	–	11.0	–
	313.15			10.1	
TAME + iso-octane	298.15	–	–	9.1	–
	313.15			8.7	
Methanol + TAME	298.15	−21.7	−15.2	6.2	19.3
	313.15	−21.7	−15.2	4.4	12.6

The reduction parameters P_i^* of the pure components are obtained from

$$P_i^* = (\alpha_i - \alpha_i^*) T \tilde{V}_i^2 \left(\kappa_{Ti} - \alpha_i^* T \frac{\Delta v_i^*}{\Delta h_i^*} \right)^{-1}, \quad i = (A, B) \tag{19}$$

$\kappa_{Ti} = (\partial \ln V_i / \partial P)_T$ is the isothermal compressibility of the pure liquids. If a non-associating component B is partner in the mixture Δv_B^*, Δh_B^*, K_B and α_B^* vanish and Eqs. (16) and (19) become more simple.

The ERAS parameters were adjusted to the experimental excess enthalpies. The properties and parameters of the pure substances are listed in Table 3. The adjustable parameters are listed in Table 4. It has been found [7], that $\Delta h_A^* = -25.1$ kJ mol^{-1} is an average

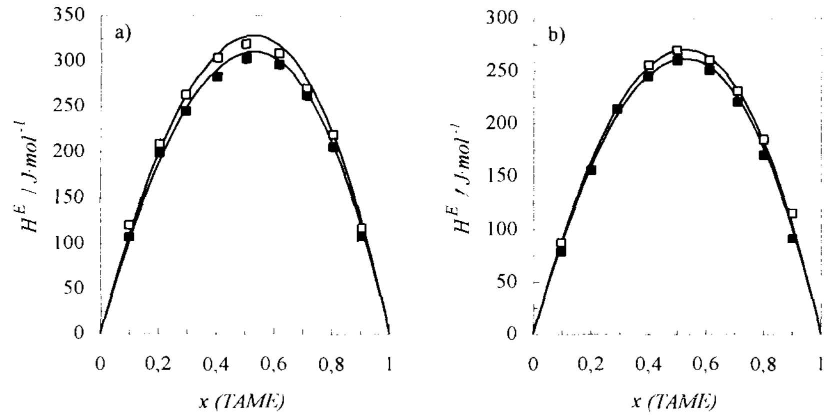

Fig. 3. ERAS model calculation for H^E of {x TAME + (1 − x)n-octane} (a) and {x TAME + (1 − x)iso-octane} (b). Experimental results: □, 298.15 K, ■, 313.15 K, ——, calculated with Eqs. (3) and (4) with parameters listed in Tables 3 and 4.

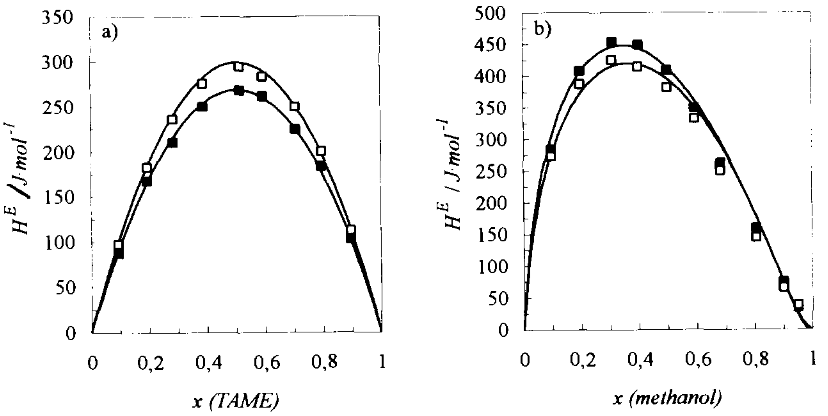

Fig. 4. ERAS model calculations for H^E of {x TAME + $(1-x)$n-heptane} (a) and {x methanol + $(1-x)$TAME} (b). Experimental results: □, 298.15 K, ■, 313.15 K, ——, calculated with Eqs. (3) and (4) with parameters listed in Tables 3 and 4

value for all alkanols. For Δv_A^* the average value of $-5.6\ \mathrm{cm^3\ mol^{-1}}$ gives good results for the mixture {methanol + TAME}.

The molar excess enthalpies calculated with the ERAS-model correspond very well with the experimental data. Figs. 3 and 4 show the curves calculated with Eqs. (3) and (4) compared to the experimental data.

5. Conclusion

The molar excess enthalpies determined in this work are positive over the whole mole fraction range with maximum values of about $450\ \mathrm{J\ mol^{-1}}$ for the mixture {methanol + TAME} at 313.15 K. For all binary {TAME + alkane} systems $(\partial H_m^E/\partial T)$is negative, for the mixture {methanol + TAME} it is positive. The ERAS model allows a theoretical interpretation of the experimental molar excess enthalpies. The predictions agree satisfactorily with the experimental data.

References

[1] E. Tusel-Langer, M. Garcia Alonso, M.A. Villamañan Olfos and R.N. Lichtenthaler, J. Sol. Chem., 20 (1990) 153–163.
[2] E. Tusel-Langer and R.N. Lichtenthaler, Ber. Bunsenges. Phys. Chem., 95 (1991) 145–152.
[3] A. Heintz, Ber. Bunsenges. Phys. Chem., 89 (1985) 172–182.
[4] A. Heintz and R.N. Lichtenthaler, Ber. Bunsenges. Phys. Chem., 83 (1979) 853–856.
[5] S. Zhu, S. Shen, G.C. Benson and B.C.-Y. Lu, J. Chem. Thermodynamics, 26 (1994) 35–39.
[6] H. Funke, M. Wetzel and A. Heintz, Pure Appl. Chem., 61 (1989) 1429–1439.
[7] H. Renon and J.M. Prausnitz, Chem. Eng. Sci., 22 (1967) 299–307

[8] H. Kehiaian and A.J. Treszczanowicz, Bull. Acad. Chim. Fr., 5 (1969) 15611568.
[9] P.J. Flory, R.A. Orwoll and A. Vrij, J. Am. Chem. Soc., 86 (1964) 3507–3514.
[10] B.E. Eichinger and P.J. Flory, Trans. Farad. Soc., 64 (1968) 2035–2052.
[11] A. Bondi, Physical Properties of Molecules, Crystals, Liquids, and Gases, Wiley, New York, 1968.