Volumetric properties of hexamethyleneimine and of its mixtures with water

Christophe Coquelet, Javeed A. Awan, Alain Valtz, Dominique Richon *

Mines ParisTech, CEP/TEP - Centre énergétique et procédés, CNRS FRE 2861, 35 Rue Saint Honoré, 77305 Fontainebleau, France

ARTICLE INFO

ABSTRACT

Densities of pure hexamethyleneimine and of its aqueous solutions have been measured at atmospheric pressure, using an Anton Paar digital vibrating tube densimeter, from 273.16 to 363.15 K and from 283.15 to 353.15 K, respectively. Acceptable representations of experimental data are found using a general correlation from Dauber et al. for pure hexamethyleneimine and using a general correlation from Bettin and Spieweck for pure water; thus indicating consistency of newly measured data. In this paper, we show the Redlich–Kister equation leads to incorrect data treatment particularly at low concentrations for systems presenting hydrophobic interactions. Thermal expansion coefficients (α^*) for the pure hexamethyleneimine (HMI) and excess thermal expansion coefficient (α^E) of the binary mixture: HMI + water at 283.15 and 298.15 K over the whole mole fraction range of water are presented and discussed in terms of the structural changes in the mixtures.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Accurate descriptions, through reliable models, of the thermodynamic properties of multi-component fluid mixtures are important for both the optimization of current industrial processes and for the optimized design of new ones. Deviations from ideality are conveniently represented by excess properties that are useful to understand the mixing state in terms of molecular interactions.

In this work, we are concerned by density measurements and data treatment, and also by calculations of thermal expansion coefficients and of excess thermal expansivities at 283.15 and 323.15 K over the whole mole fraction range for hexamethyleneimine (HMI) + water binary system. For these purposes Redlich–Kister equation [1] has been used along with other thermodynamic correlations. HMI ($C_6H_{13}N$, CAS number: 111-49-9) is intermediate compound for organic syntheses related to pharmaceuticals, agrochemicals, zeolites, dyes, rubbers, textile chemicals, corrosion inhibitors and ore-flotation processes. This chemical consists of one amino, a prefix denoting the presence of the bivalent group "–*NH*" attached to the radical part, and is usually synthesized by condensation reactions of aldehydes or ketones with simple amines.

Pure water density data from Bettin and Spieweck [2] were used for the calibration of the densimeter in the 273.15–373.15 K temper-

ature range. We have selected the Anton Paar digital vibrating tube densimeter to measure densities at atmospheric pressure of pure HMI in the 273.16–363.15 K temperature range and of binary mixtures of HMI + water in the 283.15–353.15 K temperature range. The density data measured for pure HMI are compared to data predicted through the correlation of Daubert et al. [3], in order to study the accuracy and the consistency of our density data.

Important questions have pointed out by Jacques Desnoyers (personal communication): can we consider that using the Redlich–Kister equation is sufficient to understand and explain the behaviour of the solution? Can another method be used? Moreover, excess thermal expansion values of multi-component fluid mixtures are of great interest to understand the mixing state in terms of intermolecular interactions as a function of temperature. Excess thermal expansion coefficients of two binary systems: HMI + water and DMAPA (3-dimethylamino propylamine) + water at 283.15 and 298.15 K over the whole mole fraction range are derived from the results and compared in terms of the structural changes and functional group.

2. Experimental

2.1. Materials purities and suppliers

HMI was purchased from Aldrich with a certified purity more than 99%. Ultra pure water was produced in our laboratory using commercial equipment (Millipore™, model direct Q5). HMI and water were degassed independently and mixed under partial

* Corresponding author. Tel.: +33 1 64 69 49 65; fax: +33 1 64 69 49 68.
E-mail address: dominique.richon@mines-paristech.fr (D. Richon).

vacuum. Compositions of mixtures are determined gravimetrically.

2.2. Experimental method

Density measurements have been all performed with a DMA5000 Anton Paar digital vibrating tube densimeter. Specifications given by Anton Paar for this instrument are the following: accuracy on density: $\pm 0.000005\,g\,cm^{-3}$ and on temperature: ± 0.01 K, repeatability on density: $0.000001\,g\,cm^{-3}$ and on temperature: 0.001 K. One platinum resistance thermometer with 0.01 K accuracy is used for temperature measurements. Temperature is controlled by Peltier effect.

Eq. (1) is used for relating the period of vibration, τ, to density, ρ:

$$\rho = a + b\tau^2 \tag{1}$$

where a and b are constants to be adjusted. For these purposes we have used bi-distilled and degassed water, and dry air, at 293.15 K. After calibration, resulting uncertainty is estimated lower than $0.00001\,g\,cm^{-3}$. The sample densities are then measured at thermal equilibrium for various temperatures. Procedure for preparation of mixtures is the following: first an empty $20\,cm^3$ glass bottle is airtight closed with a septum and then evacuated with the help of a vacuum pump using a needle introduced through the septum. Empty bottle is weighed, and then the less volatile component, freshly degassed by vacuum distillation, is introduced by means of a syringe. After weighing the bottle loaded with the first component, the more volatile one is added similarly and then the bottle is weighed again. All weighing are performed using an analytical
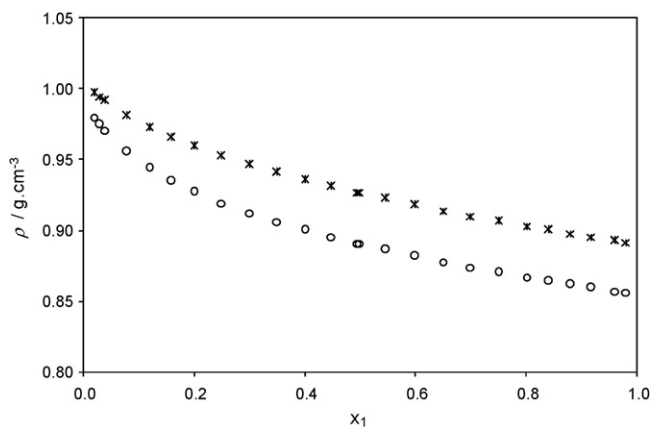

Fig. 1. Density of HMI (1) + water (2) system as a function of HMI mole fraction at atmospheric pressure and different temperatures: (*) 283.15 and (o) 323.15 K.

balance with 0.0003 g accuracy, correspondingly the uncertainty is estimated to be lower than 0.0003 for mole fractions. Maximum error resulting in the calculation of v^E is estimated to be less than $0.007\,cm^3\,mol^{-1}$.

3. Results and discussions

The density values of pure HMI measured using the DMA 5000 Anton Paar densimeter are presented as a function of temperature in Table 1 . This table also compares experimental values to calculated ones using the correlation of Daubert et al. [3]:

$$\rho = \frac{A}{B^{1+(1-(T/T_C))^C}} \times \frac{M_i}{1000} \tag{2}$$

where A, B and C are constants reported in Table 2. For HMI we have reported the parameters provided by Daubert et al. [3] and the parameters we have adjusted using our experimental data. T and T_C stand for equilibrium temperature and critical temperature, respectively. As can be seen, from both Table 1 and figure Y, the experimental and predicted data are in acceptable agreement with deviations lower than 0.06%, thus indicating the consistency of the measured density data.

The experimental density data and molar excess volume for binary mixtures of HMI + water measured at various temperatures and atmospheric pressure as a function of water mole fraction are presented in Table 3. The density data have been plotted as a function of HMI mole fraction in Fig. 1.

The excess molar volume v^E, is calculated using the following equation:

$$v^E = v - x_1 v_1^* - x_2 v_2^* \tag{3}$$

where x_1 and x_2 represent mole fractions and v_1^* and v_2^* are the molar volumes of components 1 and 2, respectively. v stands for the molar volume of mixture.

Using the density ρ, Eq. (3) can be rewritten as

$$v^E = \left[\frac{x_1 M_1 + x_2 M_2}{\rho}\right] - \frac{x_1 M_1}{\rho_1^*} - \frac{x_2 M_2}{\rho_2^*} \tag{4}$$

where M_1 and M_2 are the molar masses ρ_1^* and ρ_2^* are the densities of components (1) and (2), respectively. ρ stands for the density of the mixture.

Usually the Redlich–Kister equation [1] is applied to correlate excess molar volumes, for a binary system we have

$$v^E = x_1 x_2 \sum_i A_i (x_1 - x_2)^i, \quad i \leq 9 \tag{5}$$

Table 1
Experimental (this work) and calculated (Eq. (2)) density data of pure HMI as a function of temperature.

T (K)	ρ_{exp} (g cm^{-3})	ρ_{cal} (g cm^{-3})	T (K)	ρ_{exp} (g cm^{-3})	ρ_{cal} (g cm^{-3})
273.16	0.89881	0.89755	296.15	0.87849	0.87849
273.66	0.89836	0.89715	296.65	0.87805	0.87807
274.16	0.89792	0.89674	297.15	0.87761	0.87765
274.66	0.89748	0.89633	297.65	0.87716	0.87723
275.16	0.89704	0.89592	298.15	0.87672	0.87681
275.66	0.89660	0.89551	298.65	0.87628	0.87638
276.16	0.89616	0.89510	299.15	0.87583	0.87596
276.66	0.89572	0.89469	299.65	0.87539	0.87554
277.16	0.89528	0.89428	300.15	0.87495	0.87512
277.66	0.89484	0.89386	300.65	0.87450	0.87469
278.16	0.89440	0.89345	301.15	0.87406	0.87427
278.66	0.89396	0.89304	301.65	0.87362	0.87385
279.16	0.89351	0.89263	302.15	0.87317	0.87342
279.66	0.89307	0.89222	302.65	0.87273	0.87300
280.16	0.89263	0.89181	303.15	0.87229	0.87258
280.66	0.89219	0.89139	303.65	0.87184	0.87215
281.16	0.89175	0.89098	304.15	0.87140	0.87173
281.66	0.89131	0.89057	304.65	0.87096	0.87130
282.16	0.89087	0.89015	305.15	0.87051	0.87088
282.66	0.89042	0.88974	305.65	0.87007	0.87045
283.16	0.88998	0.88933	306.15	0.86962	0.87002
283.66	0.88954	0.88891	306.65	0.86918	0.86960
284.16	0.88910	0.88850	307.15	0.86874	0.86917
284.66	0.88866	0.88808	307.65	0.86829	0.86875
285.15	0.88822	0.88768	308.15	0.86785	0.86832
285.66	0.88777	0.88725	308.65	0.86740	0.86789
286.16	0.88733	0.88684	309.15	0.86696	0.86746
286.66	0.88689	0.88642	309.65	0.86651	0.86704
287.16	0.88645	0.88601	310.15	0.86607	0.86661
287.66	0.88600	0.88559	310.65	0.86563	0.86618
288.16	0.88556	0.88518	311.15	0.86518	0.86575
288.66	0.88512	0.88476	311.65	0.86474	0.86532
289.16	0.88468	0.88434	312.15	0.86429	0.86489
289.66	0.88423	0.88393	312.65	0.86385	0.86446
290.16	0.88379	0.88351	313.15	0.86340	0.86403
290.66	0.88335	0.88309	313.65	0.86296	0.86360
291.15	0.88291	0.88268	314.15	0.86251	0.86317
291.65	0.88247	0.88226	314.65	0.86207	0.86274
292.16	0.88203	0.88184	315.15	0.86162	0.86231
292.65	0.88158	0.88143	315.65	0.86118	0.86188
293.15	0.88115	0.88101	316.15	0.86073	0.86145
293.65	0.88071	0.88059	316.65	0.86029	0.86102
294.15	0.88026	0.88017	317.15	0.85984	0.86058
294.65	0.87982	0.87975	317.65	0.85940	0.86015
295.15	0.87938	0.87933	318.15	0.85895	0.85972
295.65	0.87894	0.87891	318.65	0.85851	0.85928
319.15	0.85806	0.85885	342.15	0.83747	0.83858
319.65	0.85761	0.85842	342.65	0.83702	0.83813
320.15	0.85717	0.85798	343.15	0.83657	0.83768
320.65	0.85672	0.85755	343.65	0.83612	0.83723
321.15	0.85628	0.85711	344.15	0.83567	0.83678
321.65	0.85583	0.85668	344.66	0.83521	0.83632
322.15	0.85539	0.85624	345.16	0.83476	0.83587
322.65	0.85494	0.85581	345.65	0.83431	0.83543
323.15	0.85449	0.85537	346.15	0.83386	0.83498
323.65	0.85405	0.85494	346.65	0.83341	0.83453
324.15	0.85360	0.85450	347.15	0.83296	0.83408
324.65	0.85315	0.85406	347.65	0.83250	0.83362
325.15	0.85271	0.85363	348.15	0.83205	0.83317
325.66	0.85226	0.85318	348.65	0.83160	0.83272
326.16	0.85181	0.85274	349.15	0.83114	0.83227
326.66	0.85137	0.85230	349.65	0.83069	0.83181
327.15	0.85092	0.85188	350.15	0.83024	0.83136
327.66	0.85047	0.85143	350.65	0.82979	0.83091
328.16	0.85003	0.85099	351.15	0.82933	0.83045
328.66	0.84958	0.85055	351.65	0.82888	0.83000
329.16	0.84913	0.85011	352.15	0.82843	0.82954
329.66	0.84869	0.84967	352.65	0.82797	0.82909
330.16	0.84824	0.84923	353.15	0.82752	0.82863
330.65	0.84779	0.84880	353.65	0.82707	0.82817
331.16	0.84735	0.84835	354.15	0.82662	0.82772
331.66	0.84690	0.84791	354.65	0.82616	0.82726
332.15	0.84645	0.84747	355.15	0.82571	0.82680
332.66	0.84600	0.84702	355.65	0.82526	0.82635
333.16	0.84555	0.84658	356.15	0.82481	0.82589

Table 1 (*Continued*)

T (K)	ρ_{exp} (g cm^{-3})	ρ_{cal} (g cm^{-3})	T (K)	ρ_{exp} (g cm^{-3})	ρ_{cal} (g cm^{-3})
333.65	0.84511	0.84615	356.65	0.82436	0.82543
334.16	0.84466	0.84570	357.15	0.82390	0.82497
334.65	0.84421	0.84526	357.65	0.82345	0.82451
335.16	0.84376	0.84481	358.15	0.82300	0.82405
335.65	0.84331	0.84438	358.65	0.82255	0.82359
336.16	0.84286	0.84392	359.15	0.82209	0.82313
336.66	0.84242	0.84348	359.65	0.82164	0.82267
337.16	0.84196	0.84303	360.15	0.82119	0.82221
337.66	0.84152	0.84259	360.65	0.82073	0.82175
338.16	0.84107	0.84214	361.15	0.82028	0.82129
338.66	0.84062	0.84170	361.65	0.81982	0.82082
339.16	0.84017	0.84125	362.15	0.81937	0.82036
339.66	0.83972	0.84080	362.65	0.81891	0.81990
340.16	0.83927	0.84036	363.15	0.81846	0.81944
340.66	0.83882	0.83991			
341.16	0.83837	0.83946			
341.65	0.83792	0.83902			

The coefficients (A_i), determined at each temperature are presented in Table 4. Five parameters have been adjusted. This table also shows the variance σ, corresponding to each fit, calculated using the following equation:

$$\sigma = \sqrt{\left[\sum \frac{(v^E - v^E_{cal})^2}{N_{exp} - P}\right]} \qquad (6)$$

where P is the number of A_n parameters and N_{exp} represents the number of experimental data. The standard deviation is quite high diplaying difficulty of representation by R–K equation (we shall see latter it is especially due to the diluted regions).

Excess molar volumes (v^E) for the HMI (1) + water (2) binary system are plotted in Fig. 2a and b as a function of water composition at different temperatures. All excess molar volumes $v^E(T)$ are negative, indicating packing effect and/or strong interactions between unlike components as expected in the investigated mixture. Following the suggestion of Desnoyers and Perron [4], the quantity v^E/x_1x_2

Table 2
Parameters of Daubert et al. equation (Eq. (2)) for HMI and water.

Compound	T_C (K)	A (kmol/m^3)	B	C
HMI[a]	624.0	0.6946	0.2508	0.270
Water[a]	647.1	5.4590	0.3054	0.081
HMI[b]	624.0	0.8927	0.2828	0.31

[a] Parameters from Daubert et al. [3].
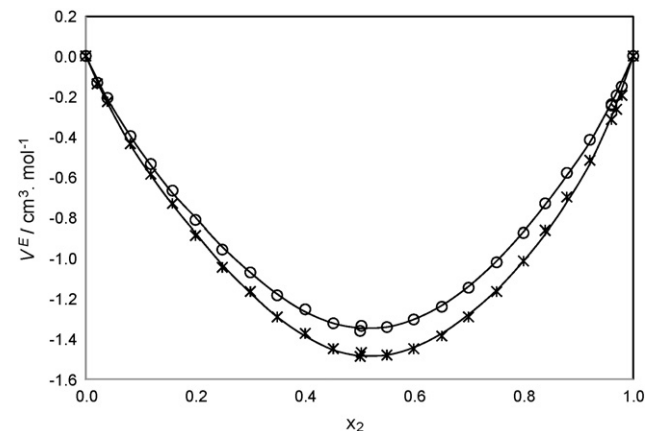[b] Parameters adjusted using our experimental data.

Fig. 2. Excess molar volume (v^E) for HMI (1) + water (2) binary system as a function of composition at different temperatures: (*) 283.15 and (o) 323.15 K.
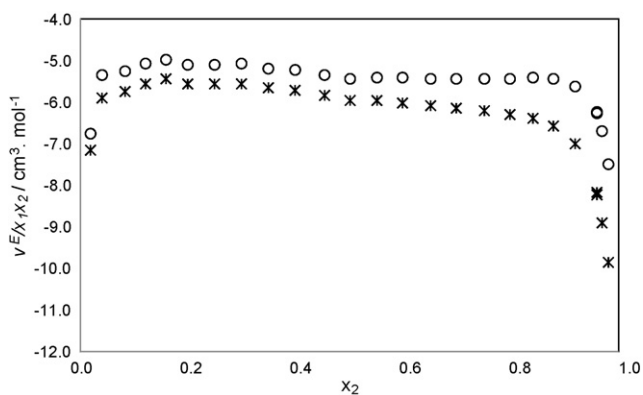
Fig. 3. $v^E/x_1 x_2$ (HMI + water system) as a function of water mole fraction at atmospheric pressure and different temperatures: (*) 283.15 and (o) 323.15 K.

was also calculated as it is more appropriate to give information on interactions at low concentrations. This thermodynamic quantity is equivalent to an apparent molar volume over the whole mole fraction range. In fact, $v^E/x_1 x_2 = v_{2,\varphi} - v_2^*/x_1 = v_{1,\varphi} - v_1^*/x_2$ where $v_{i,\varphi}$ is the apparent molar volume of i species, and tends to the two excess standard partial molar volumes $v_2^o - v_2^*$ and $v_1^o - v_1^*$ as x_2 tends to zero or 1. The trends of $v^E/x_1 x_2$ with concentration will reflect the intermolecular interactions as in the case of apparent or partial molar volumes. With hydrophobic solutes in water, $v^E/x_1 x_2$ will generally go through a minimum in the water-rich region (Franks and Desnoyers [5]). However, our results with HMI (see Fig. 3), do not display any minimum in our amine dilute region indicating that we have not worked in the high enough dilution. The Redlich–Kister equation which parameters adjusted on our experimental data in the whole range of composition behaves similarly displaying no minimum. Consequently, the real excess standard partial molar volume of HMI cannot be obtained by extrapolation of our data through the Redlich–Kister equation.

To verify the existence of the expected minimum, we have applied again the data treatment proposed by Desnoyers and Perron [4] to other systems: piperidine + water, isopropanolamine (IPA) + water and DMAPA + water, propanol + water and DMAPA + water binary systems [6–9]. The results are presented in Figs. 4–7. With piperidine, the results are similar to those obtained with HMI. With IPA and DMAPA, there is a minimum of $v^E/x_1 x_2$ in the very dilute amine concentration region. With IPA, the minimum is less pronounced than with DMAPA. The difference can be attributed to the fact that DMAPA has two amines groups while IPA has just one but one OH group. Interactions between water and OH group appear as stronger than interactions between amine group and water. With 1-propanol at 298.15 K, there is a minimum
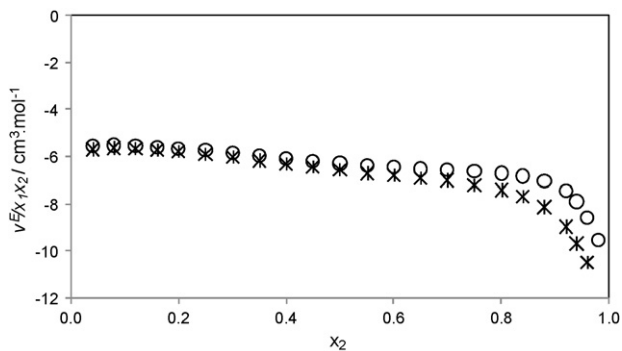
of $v^E/x_1 x_2$ in the dilute alcohol concentration region: in comparison with HMI or piperidine, result obtained with 1-propanol confirms that interactions between water and OH are stronger than interactions between amine group and water.

With HMI and piperidine, the minimum of $v^E/x_1 x_2$ probably exists. These two chemicals species have numerous CH_2 groups which favor hydrophobic interactions. Amine and alcohol groups create H-bonds with water molecules and are then in favor of hydrophobic interactions in the presence of alkyl groups. Consequently, the concentration corresponding to the minimum of

Fig. 5. $v^E/x_1 x_2$ (isopropanolamine (IPA) + water system) as a function of water mole fraction at atmospheric pressure and different temperatures: (*) 283.15 and (o) 323.15 K. Density data are from Ref. [7].
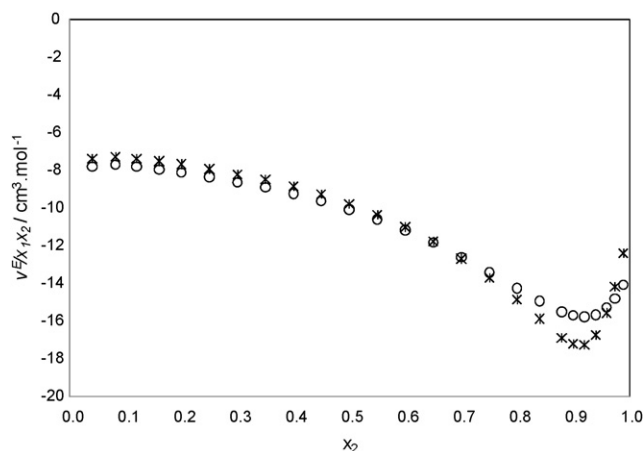
Fig. 6. $v^E/x_1 x_2$ (3-(dimethylamino) propylamine (DMAPA) + water system) as a function of water mole fraction at atmospheric pressure and different temperatures: (*) 283.15 and (o) 323.15 K. Density data are from Ref. [8].
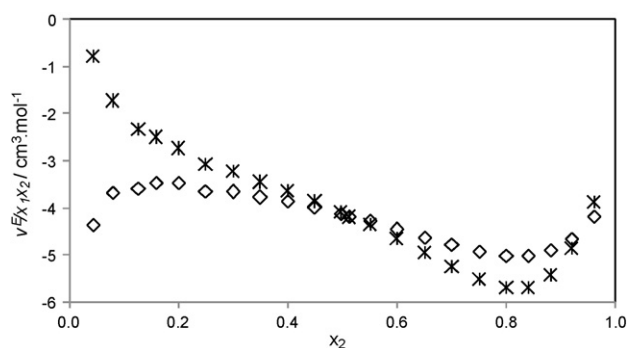

Fig. 4. $v^E/x_1 x_2$ (piperidine + water system) as a function of water mole fraction at atmospheric pressure and different temperatures: (*) 283.15 and (o) 323.15 K. Density data are from Ref. [6].
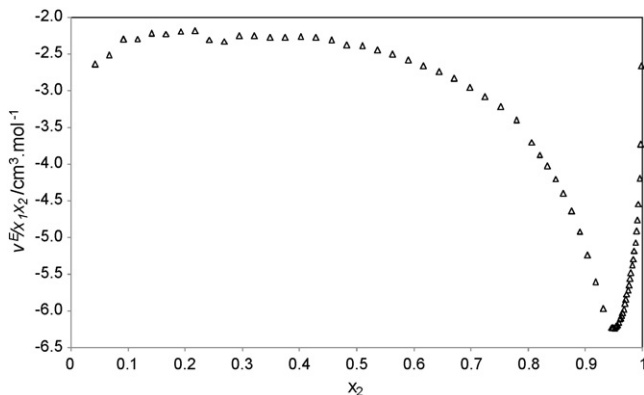

Fig. 7. $v^E/x_1 x_2$ (1-propanol + water system) as a function of water mole fraction at atmospheric pressure and at 298.15 K. Density data are from Ref. [9].

Table 3
Densities (ρ) and excess molar volumes (v^E) for HMI (1) + water (2) binary system as a function of water mole fraction.

x_2	$T = 283.15$ K		$T = 288.15$ K		$T = 293.15$ K		$T = 298.15$ K		$T = 303.15$ K	
	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})
0.0199	0.89147	-0.139_1	0.88705	-0.139_1	0.88262	-0.136_8	0.87818	-0.135_5	0.87374	-0.134_8
0.0395	0.89256	-0.224_0	0.88813	-0.222_3	0.88370	-0.219_6	0.87925	-0.216_2	0.87480	-0.214_6
0.0821	0.89527	-0.432_0	0.89084	-0.429_5	0.88639	-0.424_0	0.88194	-0.419_3	0.87747	-0.416_2
0.1198	0.89759	-0.586_0	0.89316	-0.582_6	0.88870	-0.575_2	0.88423	-0.566_7	0.87975	-0.563_1
0.1594	0.90005	-0.730_0	0.89561	-0.724_3	0.89115	-0.716_1	0.88667	-0.704_8	0.88219	-0.701_6
0.1994	0.90285	-0.886_4	0.89840	-0.878_5	0.89394	-0.869_6	0.88946	-0.856_9	0.88496	-0.852_0
0.2498	0.90632	-1.043_4	0.90188	-1.034_8	0.89741	-1.023_6	0.89292	-1.007_3	0.88842	-1.003_1
0.3000	0.90981	-1.166_1	0.90538	-1.156_2	0.90091	-1.143_4	0.89642	-1.124_5	0.89191	-1.119_4
0.3499	0.91373	-1.289_6	0.90930	-1.277_5	0.90484	-1.263_9	0.90036	-1.243_2	0.89585	-1.238_4
0.4000	0.91767	-1.373_2	0.91325	-1.359_3	0.90879	-1.343_7	0.90432	-1.320_7	0.89981	-1.315_5
0.4529	0.92226	-1.448_4	0.91786	-1.433_1	0.91342	-1.416_6	0.90896	-1.390_8	0.90446	-1.386_1
0.5008	0.92661	-1.487_3	0.92224	-1.471_0	0.91783	-1.454_0	0.91338	-1.425_4	0.90891	-1.422_1
0.5041	0.92661	-1.468_0	0.92223	-1.450_6	0.91782	-1.433_2	0.91338	-1.404_9	0.90891	-1.401_2
0.5508	0.93105	-1.476_0	0.92672	-1.458_3	0.92234	-1.439_9	0.91793	-1.409_7	0.91348	-1.406_2
0.5992	0.93570	-1.443_8	0.93142	-1.424_9	0.92709	-1.405_9	0.92272	-1.373_5	0.91831	-1.370_6
0.6500	0.94101	-1.384_7	0.93679	-1.364_1	0.93253	-1.344_5	0.92822	-1.310_1	0.92388	-1.308_7
0.6990	0.94642	-1.291_2	0.94229	-1.269_5	0.93812	-1.249_4	0.93390	-1.213_6	0.92963	-1.212_7
0.7496	0.95251	-1.162_6	0.94850	-1.139_7	0.94446	-1.119_4	0.94036	-1.082_1	0.93622	-1.083_2
0.7994	0.95933	-1.010_0	0.95551	-0.987_2	0.95164	-0.966_7	0.94771	-0.928_4	0.94373	-0.931_1
0.8398	0.96550	-0.860_3	0.96188	-0.837_5	0.95820	-0.817_2	0.95447	-0.778_6	0.95068	-0.783_2
0.8799	0.97262	-0.695_7	0.96930	-0.674_2	0.96590	-0.655_0	0.96245	-0.617_0	0.95891	-0.623_6
0.9200	0.98118	-0.515_7	0.97828	-0.496_0	0.97530	-0.479_3	0.97224	-0.442_3	0.96910	-0.452_7
0.9599	0.99153	-0.314_6	0.98932	-0.299_3	0.98699	-0.286_6	0.98454	-0.252_5	0.98198	-0.267_0
0.9600	0.99160	-0.315_8	0.98939	-0.300_5	0.98706	-0.287_8	0.98461	-0.253_4	0.98204	-0.268_0
0.9699	0.99444	-0.259_5	0.99249	-0.246_1	0.99040	-0.235_3	0.98816	-0.201_9	0.98580	-0.218_3
0.9800	0.99710	-0.193_4	0.99556	-0.184_6	0.99380	-0.176_8	0.99186	-0.145_9	0.98975	-0.164_3

x_2	$T = 308.15$ K		$T = 313.15$ K		$T = 318.15$ K		$T = 323.15$ K		$T = 333.15$ K	
	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})
0.0199	0.86929	-0.133_9	0.86483	-0.133_0	0.86037	-0.132_2	0.85590	-0.131_5	0.84692	-0.127_4
0.0395	0.87034	-0.212_3	0.86587	-0.210_1	0.86139	-0.206_7	0.85690	-0.203_3	0.84790	-0.196_8
0.0821	0.87299	-0.411_5	0.86849	-0.405_7	0.86399	-0.400_2	0.85948	-0.394_8	0.85041	-0.380_5
0.1198	0.87526	-0.557_0	0.87075	-0.550_0	0.86623	-0.542_2	0.86170	-0.534_6	0.85259	-0.516_2
0.1594	0.87768	-0.692_9	0.87316	-0.684_7	0.86863	-0.675_7	0.86408	-0.665_9	0.85493	-0.643_6
0.1994	0.88045	-0.843_2	0.87592	-0.833_9	0.87137	-0.822_9	0.86681	-0.812_3	0.85762	-0.786_7
0.2498	0.88390	-0.992_7	0.87935	-0.980_9	0.87479	-0.968_8	0.87021	-0.956_2	0.86098	-0.927_2
0.3000	0.88738	-1.107_1	0.88283	-1.094_8	0.87826	-1.081_3	0.87367	-1.067_6	0.86440	-1.035_0
0.3499	0.89132	-1.225_3	0.88676	-1.211_4	0.88218	-1.196_8	0.87758	-1.182_1	0.86828	-1.147_4
0.4000	0.89528	-1.301_2	0.89072	-1.286_4	0.88614	-1.271_0	0.88152	-1.254_1	0.87221	-1.218_5
0.4529	0.89994	-1.371_0	0.89539	-1.355_8	0.89080	-1.338_9	0.88619	-1.322_2	0.87687	-1.285_6
0.5008	0.90440	-1.406_0	0.89986	-1.390_2	0.89529	-1.373_6	0.89068	-1.356_2	0.88136	-1.318_8
0.5041	0.90440	-1.384_9	0.89986	-1.368_6	0.89528	-1.351_1	0.89068	-1.334_0	0.88135	-1.295_3
0.5508	0.90900	-1.389_8	0.90448	-1.373_1	0.89993	-1.356_2	0.89533	-1.338_0	0.88603	-1.300_0
0.5992	0.91386	-1.353_4	0.90937	-1.336_2	0.90485	-1.319_1	0.90028	-1.301_1	0.89102	-1.263_2
0.6500	0.91949	-1.291_5	0.91505	-1.274_3	0.91058	-1.257_4	0.90606	-1.240_1	0.89687	-1.202_9
0.6990	0.92532	-1.195_7	0.92096	-1.179_0	0.91655	-1.162_1	0.91210	-1.145_6	0.90303	-1.110_2
0.7496	0.93202	-1.066_3	0.92777	-1.050_3	0.92347	-1.034_4	0.91911	-1.018_4	0.91024	-0.986_5
0.7994	0.93969	-0.915_1	0.93559	-0.899_8	0.93144	-0.885_2	0.92723	-0.871_0	0.91861	-0.841_8
0.8398	0.94683	-0.768_4	0.94292	-0.754_8	0.93893	-0.741_2	0.93488	-0.728_3	0.92657	-0.702_7
0.8799	0.95531	-0.610_2	0.95163	-0.597_8	0.94787	-0.585_9	0.94403	-0.574_4	0.93613	-0.552_5
0.9200	0.96586	-0.441_5	0.96253	-0.431_3	0.95911	-0.421_9	0.95559	-0.412_9	0.94828	-0.395_9
0.9599	0.97929	-0.259_1	0.97648	-0.252_0	0.97355	-0.245_6	0.97050	-0.239_6	0.96406	-0.228_4
0.9600	0.97935	-0.260_0	0.97654	-0.253_0	0.97361	-0.246_6	0.97056	-0.240_5	0.96412	-0.229_4
0.9699	0.98330	-0.211_5	0.98066	-0.205_4	0.97790	-0.200_1	0.97501	-0.195_1	0.96888	-0.186_2
0.9800	0.98748	-0.159_1	0.98506	-0.154_6	0.98250	-0.150_6	0.97980	-0.146_8	0.97402	-0.140_3

Densities (ρ) and excess molar volumes (v^E) for HMI (1) + water (2) binary system as a function of H_2O composition

x_2	$T = 343.15$ K		$T = 348.15$ K		$T = 353.15$ K	
	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})
0.0199	0.83791	-0.124_7	0.83338	-0.124_1	0.82884	-0.123_6
0.0395	0.83884	-0.187_6	0.83430	-0.185_8	0.82973	-0.181_2
0.0821	0.84128	-0.364_0	0.83669	-0.356_4	0.83207	-0.346_2
0.1198	0.84340	-0.493_4	0.83879	-0.483_9	0.83414	-0.470_7
0.1594	0.84570	-0.617_2	0.84106	-0.604_8	0.83638	-0.588_8
0.1994	0.84834	-0.756_4	0.84367	-0.741_5	0.83895	-0.722_0
0.2498	0.85165	-0.893_2	0.84694	-0.874_6	0.84220	-0.854_6
0.3000	0.85503	-0.998_2	0.85031	-0.979_8	0.84554	-0.957_5
0.3499	0.85887	-1.108_4	0.85412	-1.088_1	0.84932	-1.064_2
0.4000	0.86276	-1.176_9	0.85799	-1.155_5	0.85318	-1.131_8

Table 3 (*Continued*)

Densities (ρ) and excess molar volumes (v^E) for HMI (1) + water (2) binary system as a function of H_2O composition

x_2	$T = 343.15\,K$		$T = 348.15\,K$		$T = 353.15\,K$	
	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})
0.4529	0.86739	-1.242_5	0.86260	-1.220_3	0.85776	-1.195_2
0.5008	0.87187	-1.275_4	0.86708	-1.253_7	0.86224	-1.229_5
0.5041	0.87187	-1.252_2	0.86707	-1.229_4	0.86222	-1.204_3
0.5508	0.87655	-1.256_7	0.87176	-1.235_0	0.86692	-1.211_1
0.5992	0.88158	-1.221_4	0.87678	-1.198_7	0.87195	-1.175_7
0.6500	0.88750	-1.163_3	0.88274	-1.142_5	0.87792	-1.119_8
0.6990	0.89376	-1.072_9	0.88904	-1.053_2	0.88427	-1.032_6
0.7496	0.90113	-0.952_2	0.89649	-0.934_7	0.89179	-0.916_1
0.7994	0.90974	-0.811_7	0.90521	-0.796_4	0.90062	-0.780_5
0.8398	0.91797	-0.676_2	0.91357	-0.663_0	0.90909	-0.648_9
0.8799	0.92791	-0.530_5	0.92342	-0.511_0	0.91878	-0.488_5
0.9200	0.94290	-0.442_8	0.93807	-0.411_3	0.93373	-0.395_4
0.9599	0.95832	-0.244_4	0.95448	-0.233_9	0.95636	-0.359_5
0.9600	0.95840	-0.245_9	0.95496	-0.244_7	0.96083	-0.462_5
0.9699	0.96325	-0.199_4	0.96276	-0.261_5	0.96260	-0.333_8
0.9800	0.96774	-0.134_4	0.96439	-0.130_9	0.96110	-0.131_1

v^E/x_1x_2 may be expected only at extremely low concentrations of HMI or piperidine.

With IPA, the minimum of v^E/x_1x_2 is around $x_2 = 0.8$, with DMAPA $x_2 = 0.9$ and with 1-propanol $x_2 = 0.95$. To find this minimum with HMI, new experimental measurements have been performed at 298.15 K and at high dilution. Table 5 presents the results which display a minimum, see Fig. 8. Unfortunately measurements had to be done close to the limit of sensitivity of our apparatus, and then with increasing uncertainties that are not fully satisfactory for x_2 higher than 0.994. Redlich–Kister equation with 9 parameters does not improve significantly the representation of the diluted region as shown in Fig. 8.

Table 4
Parameters of Redlich–Kister equation (Eq. (5)) for HMI + water binary system at various temperatures.

T (K)	A_0 (cm^3 mol)	A_1 (cm^3 mol)	A_2 (cm^3 mol)	A_3 (cm^3 mol)	A_4 (cm^3 mol)	σ (cm^3 mol)
283.15	−5.925	−0.574	1.103	−0.379	−2.778	0.016
288.15	−5.857	−0.536	1.110	−0.231	−2.599	0.015
293.15	−5.786	−0.511	1.109	−0.131	−2.420	0.014
298.15	−5.674	−0.438	1.198	0.059	−2.263	0.016
303.15	−5.656	−0.463	1.128	0.021	−2.202	0.013
308.15	−5.591	−0.443	1.136	0.071	−2.118	0.013
313.15	−5.526	−0.426	1.147	0.108	−2.050	0.012
318.15	−5.458	−0.414	1.154	0.140	−1.984	0.012
323.15	−5.387	−0.403	1.155	0.165	−1.923	0.012
333.15	−5.235	−0.392	1.177	0.193	−1.834	0.012
343.15	−5.071	−0.316	1.453	−0.107	−2.410	0.098
348.15	−4.990	−0.275	1.668	−0.237	−2.844	0.024
353.15	−4.939	0.014	2.952	−1.334	−5.689	0.066

Table 5
Densities (ρ) and excess molar volumes (v^E) for HMI (1) + water (2) binary system as a function of water composition at high HMI dilutions.

x_2	$T = 298.15\,K$	
	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})
0.95973	0.98466	-0.281_3
0.95973	0.98468	-0.281_7
0.97981	0.99190	-0.173_4
0.98510	0.99377	-0.140_0
0.98819	0.99459	-0.114_3
0.98992	0.99498	-0.098_4
0.99211	0.99543	-0.077_4
0.99403	0.99581	-0.058_5

Data treatment has been done with the Redlich–Kister equation for the interpretation of excess volume and to verify the comments from Desnoyers and Perron [4] about its inaccurate representation at infinite dilution. Strictly speaking the partial molar volumes at infinite dilution and the excess partial molar volumes at infinite dilution calculated using the parameters generated for Redlich–Kister equation can mislead, or hide strong interactions in low and high concentrations zones. Redlich–Kister data treatment with the new experimental data for HMI + water binary system does not lead to a minimum prediction. This confirms that for such a system, the Redlich–Kister equation is not convenient. Consequently, it is much better to analyze the experimental data considering v^E/x_1x_2 as a function of composition and not directly the excess volume as a function of the composition.

In order to understand the change in the solution structure during mixing, thermal expansivities are calculated for all the compositions. Thermal expansion coefficients (α^*) of pure HMI have been calculated using density data, and are presented in Table 6 as a function of temperature. They are further used to calculate excess thermal expansion coefficients of the aqueous solutions. Excess thermal expansion coefficients (α^E) and thermal expansion coefficient of the mixtures (α) at 283.15 and 298.15 K over the whole mole fraction range are calculated with Eqs. (7) and (8).

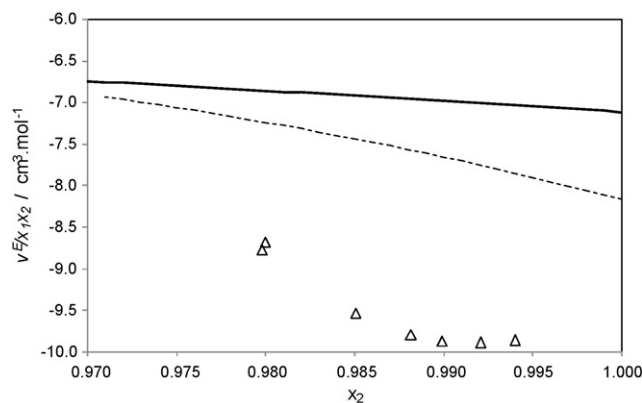$$\alpha^E = \alpha - \sum \phi_i \alpha_i^* \tag{7}$$

Fig. 8. v^E/x_1x_2 (HMI + water system) as a function of water mole fraction at atmospheric pressure and at 298.15 K. Solid line: calculated values using Redlich–Kister equation and parameters given in Table 4. Dashed line: calculated values using Redlich–Kister equation with 9 adjusted parameters.

Table 6
Thermal expansion coefficients for HMI and DMAPA from 280.16 to 363.15 K.

T (K)	HMI $\alpha^*(\times 10^3\ K^{-1})$	DMAPA[a] $\alpha^*(\times 10^3\ K^{-1})$
280.16	0.981	1.045
285.15	0.989	1.057
290.16	0.997	1.069
295.15	1.005	1.081
300.15	1.013	1.092
305.15	1.021	1.103
310.15	1.028	1.114
315.15	1.036	1.125
320.15	1.043	1.136
325.15	1.050	1.146
330.16	1.057	1.156
335.16	1.064	1.166
340.16	1.071	1.176
345.16	1.077	1.186
350.15	1.084	1.195
355.15	1.090	1.204
360.15	1.096	1.213
363.15	1.100	1.218

[a] The thermal expansion coefficients for DMAPA were calculated considering density values found in Ref. [8].

where ϕ_i is the volume fraction of component i, and (α_i^*) is the thermal expansion coefficient of pure component i. Using the classical definition of α and definition of excess volume, we finally obtained.

$$\alpha^E = \frac{1}{V}\left[\frac{\partial v^E}{\partial T} - v^E \sum \phi_i \times \alpha_i^*\right] \tag{8}$$

For a given composition, $\partial v^E/\partial T$ is determined considering the value of the excess volume for each temperature. Fig. 9 presents the HMI excess thermal expansivity as a function of water composition at two temperatures. The trends of excess thermal expansivity are quite identical for the two selected isothermsSame types of calculations have been done with DMAPA (pure DMAPA thermal expansivity is presented in Table 6). Fig. 11 presents the shape of the excess thermal expansivity as a function of water composition for DMAPA+. By comparing Figs. 9 and 10, we see a maximum for composition around $x_2 = 0.9$ for DMAPA and HMI. According to Franks and Desnoyers [5], it corresponds to a minimum of excess enthalpy. In addition, we have plotted α^E/x_1x_2 versus x_2 for HMI (Fig. 11) and DMAPA (Fig. 12). It seems that at HMI infinite dilution, this term rises to infinite values. Moreover, with DMAPA a minimum of excess thermal expansivity exists also (Fig. 10) and if we plot α^E/x_1x_2 versus x_2 (Fig. 12), we observe a sudden drop confirming the existence
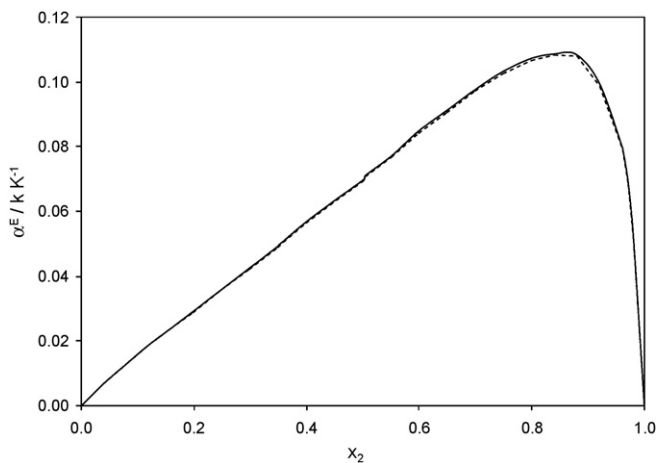
of hydrophobic interaction. Similar conclusion is possible for HMI: hydrophobic interactions occur in the HMI very dilute region. Concerning the evolution of excess thermal expansion, it can be noticed in the literature that similar behaviour exists with Tert butyl alcohol and THF [10,11]. For comparison, we have plotted on the same figure the evolution of $\partial v^E/\partial T$ for the two systems at 298.15 K (Fig. 13). The two behaviours are completely different particularly in the very
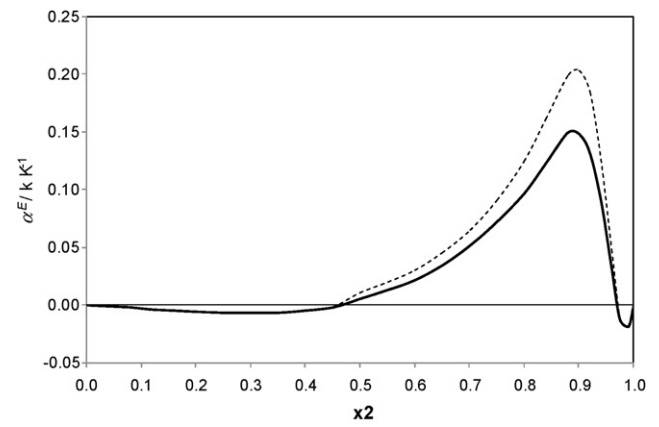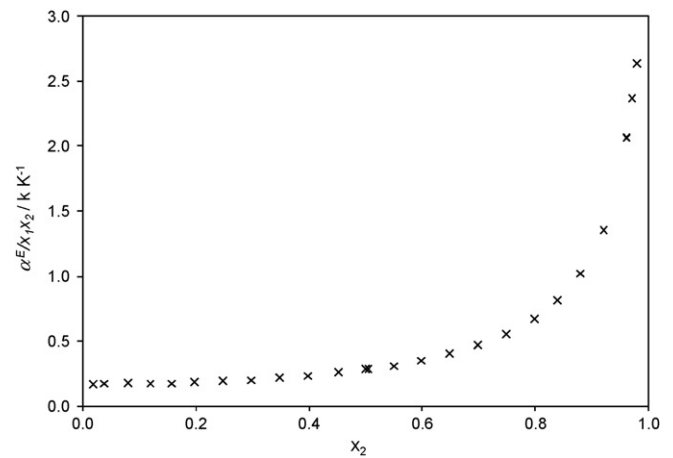

Fig. 10. Excess thermal expansion coefficients of DMAPA (1) + water system as a function of water mole fraction at atmospheric pressure. Dashed line: 283.15 K, solid line: 298.15 K.

Fig. 11. α^E/x_1x_2 (HMI (1) + water (2) system) as a function of water mole fraction at atmospheric pressure and at 298.15 K.

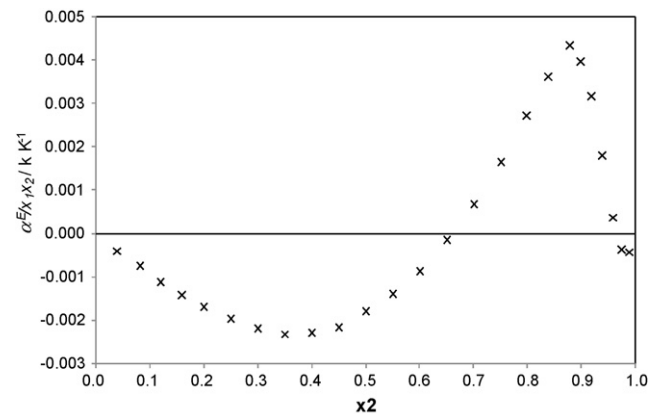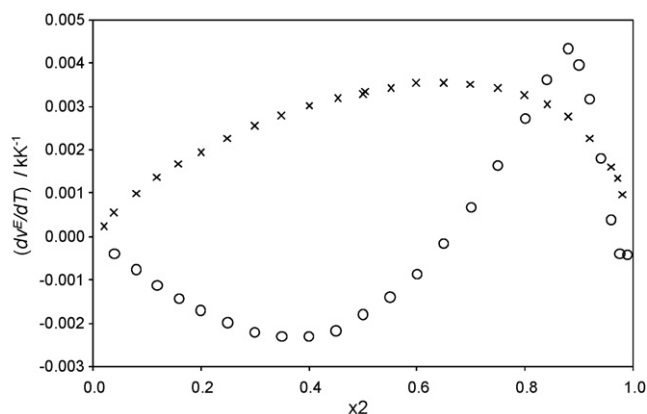**Fig. 9.** Excess thermal expansion coefficients of HMI (1) + water (2) system as a function of water mole fraction at atmospheric pressure. Dashed line: 283.15 K, solid line: 298.15 K.

Fig. 12. α^E/x_1x_2 (DMAPA (1) + water (2) system) as a function of water mole fraction at atmospheric pressure and at 298.15 K.

Fig. 13. Evolution of $\partial v^E/\partial T$ at 298.15 K for the HMI (1) + H$_2$O (2) system: ($\times$) and the DMAPA (1) + H$_2$O (2) system: (o).

dilute region (monotonous change with HMI and presence of a local minimum with DMAPA).

4. Conclusions

Densities, at atmospheric pressure, of pure hexamethyleneimine in the 273.16–363.15 K temperature range and of binary mixtures of hexamethyleneimine + water in the (283.15–353.15 K temperature range have been determined using a DMA 5000 (Anton Paar) densimeter. Excess molar volumes have been calculated displaying negative values. The limitation of Redlich–Kister equa-

tion was highlighted while comparing results for five binary systems: Redlich–Kister equation is deficient for such system in highly diluted regions. Thermal expansion coefficients (α^*) for the pure HMI and excess thermal expansion coefficient (α^E) of the HMI + water binary mixture are presented and discussed in comparison with excess thermal expansion coefficient (α^E) of the DMAPA + water where hydrophobic interactions are clearly identified.

References

[1] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 345–348.
[2] H. Bettin, F. Spieweck, PTB-Mitt 100 (1990) 195–196.
[3] T.E. Daubert, R.P. Danner, H.M. Sibel, C.C. Stebbins, Physical and Thermodynamic Properties of Pure Chemicals Data Compilation, Taylor and Francis, Washington, DC, 1997.
[4] J.E. Desnoyers, G. Perron, J. Solution Chem. 26 (1997) 749–755.
[5] F. Franks, J.E. Desnoyers, Alcohol–Water Mixtures Revisited, Water Science Reviews, vols. 171–232, Cambridge University Press, 1985, p. 171.
[6] W. Afzal, A. Valtz, C. Coquelet, D. Richon, J. Chem. Thermodyn. 40 (2008) 47–53.
[7] S. Mokraoui, A. Valtz, C. Coquelet, D. Richon, Thermochim. Acta 440 (2006) 122–128.
[8] C. Coquelet, A. Valtz, X. Courtial, D. Richon, Thermochim. Acta 448 (2006) 47–51.
[9] C. Dethlefsen, P.G. Sorensen, A. Hvidt, J. Solution Chem. 13 (1984) 191–202.
[10] O. Kiyohara, P. D'Arcy, G.C. Benson, Can. J. Chem. 56 (1978) 2803–2807.
[11] C. De Visser, G. Perron, J.E. Desnoyers, Can. J. Chem. 55 (1977) 856–862.