Thermochimica Acta, 229 (1993) 271–280
Elsevier Science Publishers B.V., Amsterdam

Excess enthalpies of binary mixtures of cycloheptane or cyclooctane with benzene or toluene or ethylbenzene at 298.15 K[1]

Emmerich Wilhelm[a,*], A. Inglese[b], J.-P.E. Grolier[c]

[a] *Institut für Physikalische Chemie, University of Vienna, Währingerstraße 42, A-1090 Vienna (Austria)*
[b] *Dipartimento di Chimica, Università degli Studi-Bari, Campus Universitario, I-7026 Bari (Italy)*
[c] *Laboratoire de Thermodynamique et Génie Chimique, Université Blaise Pascal, F-63177 Aubière (France)*

(Received and accepted 24 May 1993)

Abstract

A flow microcalorimeter of the Picker design was used to measure excess molar enthalpies H^E at 298.15 K, as a function of the mole fraction x_1 of the binary liquid mixtures cycloheptane (c-C_7H_{14}) + benzene (C_6H_6) or toluene ($C_6H_5CH_3$) or ethylbenzene ($C_6H_5C_2H_5$), and cyclooctane (c-C_8H_{16}) + benzene or toluene or ethylbenzene. The calorimeter was equipped with separators and operated in the discontinuous mode. In each series, H^E is largest for the mixture with benzene, and smallest for the mixture with ethylbenzene. For instance at $x_1 = 0.5$, $H^E/\mathrm{J\,mol^{-1}}$ is 821 for c-C_7H_{14} + C_6H_6, 624 for c-C_7H_{14} + $C_6H_5CH_3$, and 548 for c-C_7H_{14} + $C_6H_5C_2H_5$. For any given aromatic component, H^E of the mixture with cycloheptane is slightly larger than H^E of the corresponding mixture with cyclooctane. The results are discussed in terms of the simplest version of the KGB theory.

INTRODUCTION

This work forms part of our investigation into the thermodynamic properties of binary mixtures containing alicyclic compounds c-C_cH_{2c} as one component [1–3]. This line of research was initiated primarily to obtain information on the influence of the ring size c of c-C_cH_{2c} on the thermodynamic mixing quantities, which is of vital interest for our work on mixtures containing cyclic mono- and diethers [4–12]. Here, we report excess molar enthalpies at 298.15 K of the binary liquid mixtures cycloheptane (c-C_7H_{14}) + benzene (C_6H_6) or +toluene ($C_6H_5CH_3$) or +ethyl-

---

* Corresponding author.

[1] Presented at the Tenth Ulm Conference, Ulm, Germany, 17–19 March 1993.

benzene ($C_6H_5C_2H_5$), and cyclooctane (c-C_8H_{16}) + benzene or +toluene or +ethylbenzene. A preliminary discussion of our results in terms of the simplest version of the Kehiaian–Guggenheim–Barker (KGB) theory [13] is presented.

EXPERIMENTAL

Cycloheptane and cyclooctane were from Aldrich with purities of 98% and 99 + %, respectively, while the aromatics were puriss. p.a. quality from Fluka, i.e. with purities >99.5%. The liquids were carefully dried with a molecular sieve (Union Carbide, Type 4A, beads) and stored in the dark.

Excess molar enthalpies H^E were determined with a flow microcalorimeter of the Picker design (from Setaram) equipped with separators and operated in the discontinuous mode. The H^E value at any given composition was obtained as usual [14–16] from the equation

$$H^E = (x_1 V_1^* + x_2 V_2^*) V_Z I f^{-1} (L/l) \tag{1}$$

where x_1 and $x_2(=1-x_1)$ designate the mole fractions of components 1 (alicyclic) and 2 (aromatic), respectively, V_1^* and V_2^* are the molar volumes of the pure liquids, $V_Z I$ is the electric power dissipated by the Zener diode during a separate electric calibration run (Joule effect), L/l is the ratio of the distance of the recorder trace from the base line (obtained at steady state mixing conditions) to the distance corresponding to the calibration experiment, and f is the total flow rate, i.e. the sum of the individual flow rates of the two micropumps, approximately $8 \times 10^{-9}\,\mathrm{m^3\,s^{-1}}$. The calorimeter was thermostatted to about ±0.002 K, as verified with a quartz thermometer (Hewlett Packard, model 2801A). The maximum inaccuracy of the temperature readings is less than ±0.005 K. For details, we refer readers to our earlier articles. All excess molar enthalpies are based on the relative atomic mass table of IUPAC (1986) [17].

The performance of the calorimeter was routinely controlled by measuring the H^E value at 298.15 K of selected test mixtures, e.g. benzene + cyclohexane or tetrachloromethane + benzene, over the entire composition range. Agreement with recommended literature data [18] was always satisfactory, that is to say, within about 1% over most of the composition range.

RESULTS AND DISCUSSION

Experimental results for the excess molar enthalpies at 298.15 K and atmospheric pressure are given in Table 1, while graphical representations are provided by Figs. 1 and 2. For each of the six systems, experimental

TABLE 1

Excess molar enthalpies H^E for cycloheptane + benzene or toluene or ethylbenzene, and cyclooctane + benzene or toluene or ethylbenzene at 298.15 K and atmospheric pressure

x_1	$H^E/(\mathrm{J\,mol^{-1}})$	x_1	$H^E/(\mathrm{J\,mol^{-1}})$	x_1	$H^E/(\mathrm{J\,mol^{-1}})$
x_1c-C_7H_{14} + $x_2C_6H_6$					
0.0311	98.3	0.3535	761.5	0.7219	657.9
0.1019	323.1	0.4361	810.9	0.8984	320.4
0.1992	555.3	0.5214	820.9		
0.2734	676.8	0.6189	773.7		
x_1c-C_7H_{14} + $x_2C_6H_5CH_3$					
0.0369	73.7	0.3102	522.0	0.7563	492.4
0.0710	145.2	0.3952	585.9	0.8139	417.3
0.1195	245.6	0.4803	618.0	0.9136	236.4
0.1477	301.0	0.5656	622.3		
0.2292	428.3	0.6600	582.1		
x_1c-C_7H_{14} + $x_2C_6H_5C_2H_5$					
0.0423	73.7	0.3412	478.5	0.7814	420.3
0.0808	143.8	0.4294	528.0	0.8344	356.4
0.1351	237.8	0.5157	548.8	0.9241	200.6
0.1664	288.4	0.6000	544.4		
0.2551	400.1	0.6909	502.3		
x_1c-C_8H_{16} + $x_2C_6H_6$					
0.0281	98.8	0.2534	660.5	0.7088	676.9
0.0545	190.5	0.3303	749.0	0.7676	585.0
0.0929	313.4	0.4110	804.3	0.8887	328.8
0.1157	382.6	0.4957	818.4		
0.1833	542.3	0.5944	780.0		
x_1c-C_8H_{16} + $x_2C_6H_5CH_3$					
0.0334	70.6	0.2886	494.6	0.7368	483.2
0.0645	137.6	0.3709	557.1	0.7979	408.8
0.1091	229.6	0.4548	589.5	0.9051	209.3
0.1352	282.5	0.5402	596.9		
0.2115	403.5	0.6366	564.0		
x_1c-C_8H_{16} + $x_2C_6H_5C_2H_5$					
0.0383	65.1	0.3185	451.4	0.7633	415.1
0.0735	129.3	0.4044	502.1	0.8197	349.9
0.1236	219.4	0.4900	529.1	0.9166	180.9
0.1526	268.4	0.5750	527.1		
0.2360	374.6	0.6686	490.0		

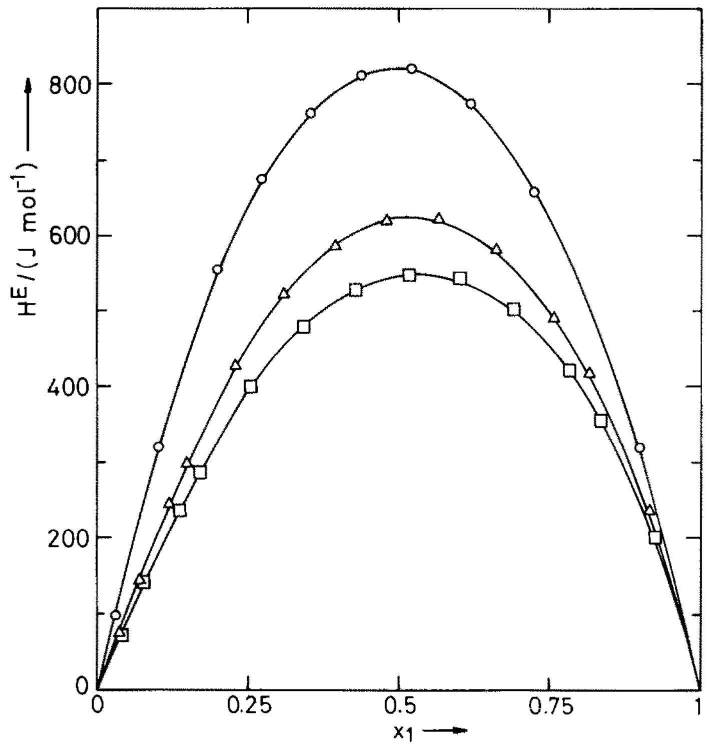

Fig. 1. Excess molar enthalpies H^E at 298.15 K. Experimental results: ○, x_1c-C_7H_{14} + $x_2C_6H_6$; △, x_1c-C_7H_{14} + $x_2C_6H_5CH_3$; □, x_1c-C_7H_{14} + $x_2C_6H_5C_2H_5$. The curves (—) were calculated from eqn. (2) with parameters A_i from Table 2.

excess molar enthalpies were fitted by unweighted least-squares polynomial regression according to

$$H^E/(J\ mol^{-1}) = x_1x_2\sum_{i=0}^{k} A_i(x_1 - x_2)^i \qquad (2)$$

where x_1 denotes the mole fraction of the cycloalkane. The coefficients A_i and the corresponding standard deviations σ are given in Table 2. These coefficients were used to obtain the calculated curves shown in the figures.

Excess partial molar quantities may easily be derived from eqn. (2). In particular, their infinite dilution values are given by

$$\bar{H}_1^{E,\infty} = \lim_{x_1\to 0} (H^E/x_1x_2) = \sum_{i=0}^{k} A_i(-1)^i \qquad (3)$$

and

$$\bar{H}_2^{E,\infty} = \lim_{x_2\to 0} (H^E/x_1x_2) = \sum_{i=0}^{k} A_i \qquad (4)$$

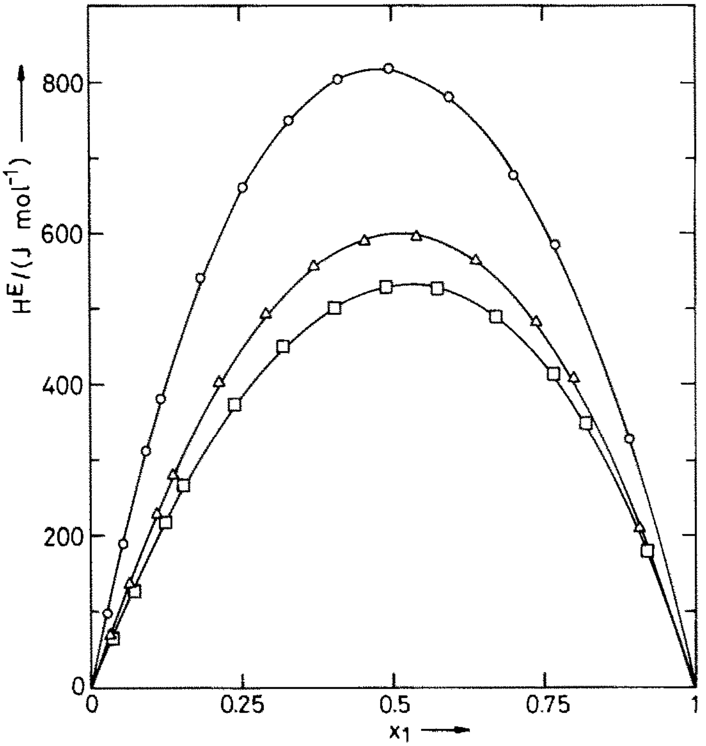

Fig. 2. Excess molar enthalpies H^E at 298.15 K. Experimental results: ○, x_1c-C_8H_{16} + $x_2C_6H_6$; △, x_1c-C_8H_{16} + $x_2C_6H_5CH_3$; □, x_1c-C_8H_{16} + $x_2C_6H_5C_2H_5$. The curves (—) were calculated from eqn. (2) with parameters A_i from Table 2.

TABLE 2

Coefficients A_i and standard deviations σ for least-squares representation of H^E by eqn. (2) at 298.15 K

Mixture	A_0	A_1	A_2	A_3	σ
x_1c-C_7H_{14} + $x_2C_6H_6$	3283.4	−87.4	334.1		6.4
x_1c-C_7H_{14} + $x_2C_6H_5CH_3$	2494.1	161.6	206.8	369.9	3.9
x_1c-C_7H_{14} + $x_2C_6H_5C_2H_5$	2193.2	230.8	279.7	384.3	3.1
x_1c-C_8H_{16} + $x_2C_6H_6$	3268.2	−240.5	418.5		4.0
x_1c-C_8H_{16} + $x_2C_6H_5CH_3$	2407.8	91.3	91.0		5.9
x_1c-C_8H_{16} + $x_2C_6H_5C_2H_5$	2130.3	227.8	132.8		5.6

TABLE 3

Excess partial molar enthalpies $\bar{H}_1^{E,\infty}$ and $\bar{H}_2^{E,\infty}$ at infinite dilution at 298.15 K

Mixture	$\bar{H}_1^{E,\infty}/(\mathrm{kJ\ mol^{-1}})$	$\bar{H}_2^{E,\infty}/(\mathrm{kJ\ mol^{-1}})$
x_1c-C_7H_{14} + $x_2C_6H_6$	3.70	3.53
x_1c-C_7H_{14} + $x_2C_6H_5CH_3$	2.17	3.23
x_1c-C_7H_{14} + $x_2C_6H_5C_2H_5$	1.86	3.09
x_1c-C_8H_{16} + $x_2C_6H_6$	3.93	3.45
x_1c-C_8H_{16} + $x_2C_6H_5CH_3$	2.41	2.59
x_1c-C_8H_{16} + $x_2C_6H_5C_2H_5$	2.04	2.49

Table 3 summarizes the $\bar{H}_i^{E,\infty}$ values for all six systems at 298.15 K.

All the excess enthalpies are positive, and the curves of H^E versus x_1 are fairly symmetrical, with maximum H^E values being near $x_1 = 0.5$. In each series, H^E is largest for the mixture with benzene and smallest for the mixture with ethylbenzene. For any given aromatic component, H^E of the mixture with cycloheptane is slightly larger than H^E of the corresponding mixture with cyclooctane.

Comparison of our H^E values with literature data is only possible for cycloheptane + benzene or toluene, and cyclooctane + benzene or toluene [19]. For the cycloheptane systems, the excess enthalpies reported by Watson et al. [19] are smaller than our results. Specifically, for equimolar solutions, $H^E(x_1 = 0.5)/\mathrm{J\ mol^{-1}}$ is 821 for c-C_7H_{14} + C_6H_6 and 624 for c-C_7H_{14} + $C_6H_5CH_3$, while Watson et al. [19] determined 758 and 588, respectively. The differences between these two data sets clearly exceed the combined estimates of experimental error. For c-C_8H_{16} + C_6H_6, we obtained $H^E(x_1 = 0.5)/\mathrm{J\ mol^{-1}} = 817$, while Watson et al. [19] report 797, i.e. about 2.4% lower. However, for c-C_8H_{16} + $C_6H_5CH_3$, their values are somewhat larger (by about 2.6%) than ours: $H^E(x_1 = 0.5)/\mathrm{J\ mol^{-1}} = 602$, compared to 618 from Watson et al. [19]. No other literature results could be found.

A preliminary, semi-quantitative discussion of our results for H^E is perhaps best conducted in terms of the KGB (Kehiaian–Guggenheim–Barker) group contribution theory [13, 20] in its simplest version, that is to say along the lines of refs. 16 and 21. In the random-mixing approximation to the KGB theory, the excess enthalpy is given by

$$H^E = \frac{1}{2}\left(\sum_i q_i x_i\right)\sum_i \sum_j \xi_i \xi_j h_{ij} \tag{5}$$

$$h_{ij} = -\frac{1}{2}\sum_s \sum_t (\alpha_{s,i} - \alpha_{s,j})(\alpha_{t,i} - \alpha_{t,j})h_{s,t} \tag{6}$$

where q_i is the relative surface of molecular species i (referred to a suitably selected yet arbitrary scaling surface), and h_{ij} is a molar enthalpic interaction parameter. In turn, this quantity is directly related to the molar interchange enthalpies $h_{s,t}$ characterizing the interaction between the various group surfaces $q_{s,i}$, $q_{s,j}$, $q_{t,i}$ and $q_{t,j}$ of type s and type t on species i and j, respectively. The molecular surface fraction of type s on species i is defined by

$$\alpha_{s,i} = q_{s,i}/q_i \tag{7}$$

$$\sum_s \alpha_{s,i} = 1 \tag{8}$$

and

$$\xi_i = q_i x_i \Big/ \sum_i q_i x_i \tag{9}$$

with corresponding relations for quantities referring to species j.

Table 4 contains all the relevant relative molecular group surfaces

$$q_g = A_g/A_{CH_4} \tag{10}$$

where A_g denotes the van der Waals surface of the group [22], and the arbitrarily selected scaling surface $A_{CH_4} = 0.289 \times 10^6\ m^2\ mol^{-1}$ is the molecular van der Waals surface of methane [13, 16]. The total relative molecular surface of component i is then

$$q_i = \sum_g q_{g,i} \tag{11}$$

In this work, component 1 is always a cycloalkane, which is a homogeneous species with $\alpha_{cy,1} = 1$ (the subscript cy signifies "alicyclic surface"). Thus

TABLE 4

Increments of relative molecular group surfaces $q_g = A_g/A_{CH_4}$ and total relative molecular surface $q = \sum q_g$ of some alicyclic and aromatic compounds calculated by Bondi's method [22]; $A_{CH_4} = 0.289 \times 10^6\ m^2\ mol^{-1}$

Group	q_g	Substance	q
$-CH_3$	0.73356	c-C_6H_{12}	2.6056
$-CH_2-_{aliphatic}$	0.46713	c-C_7H_{14}	3.0398
$-CH_2-_{alicyclic}$	0.43426	c-C_8H_{16}	3.4741
$-H_{aliphatic}$	0.26644	C_6H_6	2.0796
$-C_6H_5$	1.84429	$C_6H_5CH_3$	2.5779
$-H_{aromatic}$	0.23528	$C_6H_5C_2H_5$	3.0450

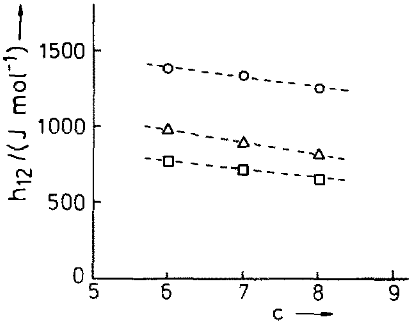

Fig. 3. Plot of the molar enthalpic interaction parameter h_{12} (at 298.15 K) against ring size c of the alicyclic hydrocarbon c-C_cH_{2c} for the series: ○, c-C_cH_{2c} + C_6H_6; △, c-C_cH_{2c} + $C_6H_5CH_3$; □, c-C_cH_{2c} + $C_6H_5C_2H_5$. The values for the cyclohexane systems ($c = 6$) were taken from the literature [18, 24, 25] as described in the text.

we obtain [16, 21, 23]

$$h_{12} = -\frac{1}{2}\sum_{s}\sum_{t} \alpha_{s,2}\alpha_{t,2}h_{s,t} + \sum_{s\neq \mathrm{cy}} \alpha_{s,2}h_{s,\mathrm{cy}} \tag{12}$$

which quantity should be independent of ring-size c within any series of type c-C_cH_{2c} + Y, irrespective of the chemical nature of component 2, i.e. irrespective of whether Y is a homogeneous or heterogeneous molecule.

Figure 3 shows h_{12} at 298.15 K plotted as a function of c for the three series ($6 \leq c \leq 8$) with Y being either benzene, or toluene or ethylbenzene. The parameter h_{12} was evaluated via eqn. (5) from the experimental values of $H^E(x_1 = 0.5)$ in conjunction with the relative molecular surfaces taken from Table 4. Experimental data concerning the mixtures with cyclohexane were taken from Stokes et al. [18], from Hsu and Clever [24], and from Murakami and Fujishiro [25]. In contrast to the prediction of the simple KGB approach, in each of these three series the enthalpic interaction parameter decreases with increasing ring size c in a rather similar manner. In the case of systems with n-alkanes, i.e. n-C_lH_{2l+2} + Y, such a decrease of the interaction parameter has been tentatively discussed in terms of the creation of order of some sort in the mixture [26–28].

In the zeroth approximation to the KGB theory, the form of any curve H^E versus x_1 is completely determined by the geometrical surface parameters q_i. From eqn. (5) it follows that the excess partial molar enthalpy of component i at infinite dilution in a binary mixture is given by

$$\bar{H}_i^{E,\infty} = q_i h_{12} \tag{13}$$

Thus, for any given series c-C_cH_{2c} + Y, $\bar{H}_2^{E,\infty}$ should be independent of ring size c, which is at variance with the experimental results given in Table 3.

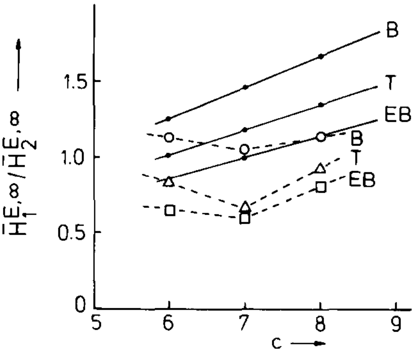

Fig. 4. Ratio of the experimental excess partial molar enthalpies $\bar{H}_1^{E,\infty}/\bar{H}_2^{E,\infty}$ plotted against ring size c of the alicyclic hydrocarbon c-C_cH_{2c} for the series B: ○, c-C_cH_{2c} + C_6H_6; series T: △, c-C_cH_{2c} + $C_6H_5CH_3$; series EB: □, c-C_cH_{2c} + $C_6H_5C_2H_5$. For convenience, the points are connected by broken lines. The values for the cyclohexane system ($c = 6$) were taken from the literature [18, 24, 25]. The ratio $\bar{H}_1^{E,\infty}/\bar{H}_2^{E,\infty}$ for c-C_6H_{12} + $C_6H_5C_2H_5$ obtained from the data of ref. 25 has a significantly larger uncertainty than the other ratios. The solid lines connect theoretical zeroth-order KGB results calculated via eqn. (11) (—•—).

The ratio of the excess partial molar enthalpies at infinite dilution is given by

$$\bar{H}_1^{E,\infty}/\bar{H}_2^{E,\infty} = q_1/q_2 \tag{14}$$

independent of h_{12}. In Fig. 4 the experimental and calculated ratios of $\bar{H}_1^{E,\infty}/\bar{H}_2^{E,\infty}$ are compared for the three series c-C_cH_{2c} + C_6H_6, c-C_cH_{2c} + $C_6H_5CH_3$, and c-C_cH_{2c} + $C_6H_5C_2H_5$. While the relative sequence of the experimental results confirms the theory, the overall accord is less than satisfactory [16, 20, 21]. As pointed out by Kehiaian [20], the situation may be greatly improved through use of an extended quasi-chemical group contribution model (DISQUAC).

ACKNOWLEDGEMENTS

Financial support received from the Austrian–French programme on scientific and technical cooperation is gratefully acknowledged by E.W. and J.-P.E.G.

REFERENCES

1 E. Wilhelm, A. Inglese and J.-P.E. Grolier, J. Chem. Eng. Data, 28 (1983) 202.
2 E. Wilhelm, A. Inglese and J.-P.E. Grolier, J. Chem. Eng. Data, 34 (1989) 332.
3 E. Wilhelm, A. Inglese and J.-P.E. Grolier, Thermochim. Acta, 187 (199) 113.
4 A. Inglese, E. Wilhelm, J.-P.E. Grolier and H.V. Kehiaian, J. Chem. Thermodyn., 12 (1980) 217.
5 A. Inglese, E. Wilhelm, J.-P.E. Grolier and H.V. Kehiaian, J. Chem. Thermodyn., 12 (1980) 1047.

6 A. Inglese, E. Wilhelm, J.-P.E. Grolier and H.V. Kehiaian, J. Chem. Thermodyn., 13 (1981) 229.
7 E. Wilhelm, A. Inglese, J.-P.E. Grolier and H.V. Kehiaian, J. Chem. Thermodyn., 14 (1982) 33.
8 E. Wilhelm, A. Inglese, J.-P.E. Grolier and H.V. Kehiaian, J. Chem. Thermodyn., 14 (1982) 517.
9 J.-P.E. Grolier, A. Inglese and E. Wilhelm, J. Chem. Eng. Data, 27 (1982) 333.
10 A. Inglese, J.-P.E. Grolier and E. Wilhelm, J. Chem. Eng. Data, 28 (1983) 124.
11 J.-P.E. Grolier, A. Inglese and E. Wilhelm, J. Chem. Thermodyn., 16 (1984) 67.
12 A. Inglese, J.-P.E. Grolier and E. Wilhelm, Fluid Phase Equilibria, 15 (1984) 287.
13 H.V. Kehiaian, J.-P.E. Grolier and G.C. Benson, J. Chim. Phys., 75 (1978) 1031.
14 J.-P.E. Grolier, G.C. Benson and P. Picker, J. Chem. Thermodyn., 7 (1975) 89.
15 E. Wilhelm, Ber. Bunsenges. Phys. Chem., 81 (1977) 1150.
16 E. Wilhelm, A. Inglese, A.H. Roux and J.-P.E. Grolier, Fluid Phase Equilibria, 34 (1987) 49.
17 IUPAC, Pure Appl. Chem., 58 (1986) 1677.
18 R.H. Stokes, K.N. Marsh and R.P. Tomlins, J. Chem. Thermodyn., 1 (1969) 211. See also K.N. Marsh, Int. DATA Ser., Sel. Data Mixtures, Ser. A, (1973) p. 2 and 3.
19 A.E.P. Watson, I.A. McLure, J.E. Bennett and G.C. Benson, J. Phys. Chem., 69 (1965) 2753. See also G.C. Benson, Int. DATA Ser., Sel. Data Mixtures, Ser. A, (1985) p. 81, 82, 84, 85.
20 H.V. Kehiaian, Pure Appl. Chem., 57 (1985) 15.
21 A.H. Roux, J.-P.E. Grolier, A. Inglese and E. Wilhelm, Ber. Bunsenges. Phys. Chem., 88 (1984) 986.
22 A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968.
23 E. Wilhelm, A. Inglese, J.-P.E. Grolier and H.V. Kehiaian, Thermochim. Acta, 31 (1979) 85.
24 K.-Y. Hsu and H.L. Clever, J. Chem. Thermodyn., 7 (1975) 435. See also Int. DATA Ser., Sel. Data Mixtures, Ser. A, (1975) 10.
25 S. Murakami and R. Fujishiro, Bull. Chem. Soc. Jpn., 40 (1967) 1784.
26 J.-P.E. Grolier, A. Inglese, A.H. Roux and E. Wilhelm, in S.A. Newman (Ed.), Chemical Engineering Thermodynamics, Ann Arbor Science Publishers, Ann Arbor, MI, 1982, p. 483.
27 E. Wilhelm, Thermochim. Acta, 94 (1984) 47.
28 S.N. Bhattacharyya, M. Costas, D. Patterson and H.V. Tra, Fluid Phase Equilibria, 20 (1985) 27.