Thermochimica Acta, 187 (1991) 113–120
Elsevier Science Publishers B.V., Amsterdam

EXCESS ENTHALPIES OF BINARY MIXTURES CONTAINING EITHER METHYLCYCLOPENTANE OR METHYLCYCLOHEXANE

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

[a]*Institut für Physikalische Chemie, Universität Wien, Währingerstraße 42, A-1090 Wien, Austria*

[b]*Dipartimento di Chimica, Università di Bari, Campus Universitario, I-70126 Bari, Italy*

[c]*Laboratoire de Thermodynamique et Cinétique Chimique, Université Blaise Pascal, F-63177 Aubière, France*

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 mole fraction, of the mixtures methylcyclopentane ($c\text{-}C_5H_9CH_3$) + cyclopentane ($c\text{-}C_5H_{10}$), and + methylcyclohexane ($c\text{-}C_6H_{11}CH_3$), and of methylcyclohexane + n-heptane ($n\text{-}C_7H_{16}$), + n-decane ($n\text{-}C_{10}H_{22}$), + cyclopentane, + benzene (C_6H_6), and + tetrachloromethane (CCl_4). The calorimeter was equipped with separators and operated in the discontinuous mode. The H^Es of the first-named three systems are negative, those of the remaining four are all positive. At equimolar composition, $H^E(x_1=0.5)/J.mol^{-1}$ ranges from -113 for ($c\text{-}C_5H_9CH_3$ + $c\text{-}C_5H_{10}$) to + 792 for ($c\text{-}C_6H_{11}CH_3$ + C_6H_6).

1. INTRODUCTION

In a series of investigations,(1-9) we reported excess molar enthalpies H^E, excess molar heat capacities C_p^E at constant pressure, and excess molar volumes V^E of binary liquid mixtures composed of either a five- or a six-membered cyclic ether and various second components. In order to obtain more information as to the influence of ring size upon thermodynamic mixing quantities, we also measured H^E of mixtures containing either cycloheptane or cyclooctane,(10) and C_p^E and V^E of mixtures containing *trans, trans, cis*-1,5,9-cyclododecatriene.(11) As a sequel to these investigations we present here excess molar enthalpies at 298.15 K of the binary liquid mixtures methylcylopentane ($c\text{-}C_5H_9CH_3$) + cyclopentane

0040-6031/91/$03.50

(c-C_5H_{10}), and + methylcyclohexane (c-$C_6H_{11}CH_3$), and of methylcyclohexane + n-heptane (n-C_7H_{16}), + n-decane (n-$C_{10}H_{22}$), + cyclopentane, + benzene (C_6H_6), and + tetrachloromethane (CCl_4). Contacts were maintained with Kohler's group in Bochum, who also studied the effect of addition of a methyl group to the cyclopentane and cyclohexane ring on excess properties of their mixtures with n-alkanes.(12-15)

2. EXPERIMENTAL

All liquids were of the best quality available from Fluka, that is of puriss. quality (n-heptane, cyclopentane, methylcyclopentane, methylcylohexane, benzene, tetrachloromethane) or purum quality (n-decane: olefin free, purity >99%). They were carefully dried with molecular sieve (Union Carbide Type 4A, beads, from Fluka) and stored in the dark.

Excess molar enthalpies H^E were measured with a flow microcalorimeter of the Picker design (from Setaram) equipped with separators and operated in the discontinuous mode. The calorimeter was thermostatted to about ± 0.002 K as checked with a quartz thermometer (Hewlett-Packard, model 2801A). The maximum inaccuracy of the temperature readings is less than ± 0.005 K. Before being transferred to the separators, all liquids were degassed. H^E at any given composition was obtained as usual (16-18) from

$$H^E = (x_1V_1^* + x_2V_2^*)V_ZIL/(\ell f). \qquad (1)$$

Here x_1 and $x_2 = 1 - x_1$ designate the mole fractions of component 1 and 2, respectively, V_1^* and V_2^* are the molar volumes of the pure liquids, V_ZI 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. For details we refer to our earlier articles. The performance of the calorimeter was routinely controlled by measuring H^E at 298.15 K of selected test mixtures, say (benzene + cyclohexane), over the entire composition range. Agreement with recommended literature data(19) was always satisfactory, that is to say within 1% over most of the composition range. All excess molar enthalpies are based on the relative atomic mass table of IUPAC, 1986.(20)

3. RESULTS AND DISCUSSION

Experimental results for the excess molar enthalpies at 298.15 K are given in Table 1, while graphical representations are provided by Figs. 1 and 2. For each of the seven mixtures, H^E was fitted with a smoothing function of Redlich-Kister type, i.e.

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

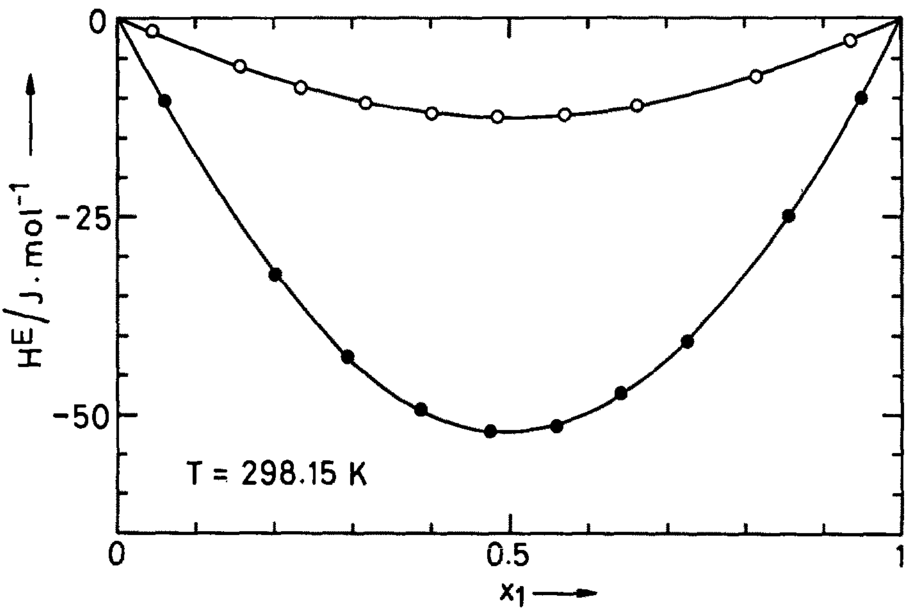

Fig.1. Excess molar enthalpies H^E at 298.15 K.Experimental results: ○, $\{x_1c\text{-}C_5H_9CH_3 + x_2c\text{-}C_5H_{10}\}$; ●, $\{x_1c\text{-}C_5H_9CH_3 + x_2c\text{-}C_6H_{11}CH_3\}$; ——, calculated from eqn.(2) with coefficients from Table 2.

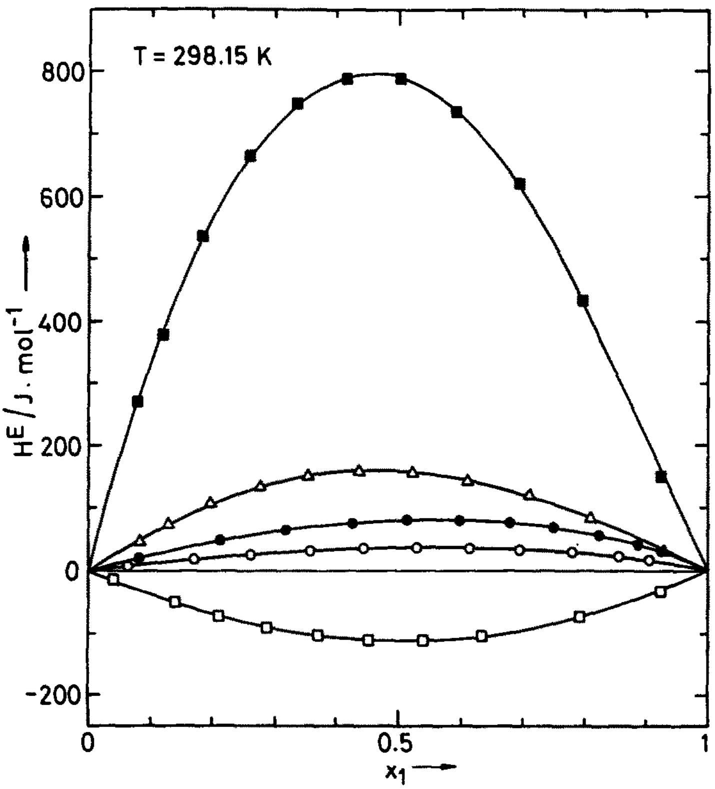

Fig.2. Excess molar enthalpies H^E at 298.15 K. Experimental results: ○, $\{x_1c\text{-}C_6H_{11}CH_3 + x_2n\text{-}C_7H_{16}\}$; ●, $\{x_1c\text{-}C_6H_{11}CH_3 + x_2n\text{-}C_{10}H_{22}\}$; □, $\{x_1c\text{-}C_6H_{11}CH_3 + x_2c\text{-}C_5H_{10}\}$; ■, $\{x_1c\text{-}C_6H_{11}CH_3 + x_2C_6H_6\}$; △, $\{x_1c\text{-}C_6H_{11}CH_3 + x_2CCl_4\}$; ——, calculated from eqn.(2) with coefficients from Table 2.

The coefficients A_i and the corresponding standard deviations s are shown in Table 2. These coefficients were used to obtain the calculated curves in the figures.

Only for methylcyclohexane + n-heptane,(21-25) + cyclopentane,(26) + benzene(27,28) and + tetrachloromethane(29) could we find published results on H^E. For $\{x_1C_6H_{11}CH_3 + x_2n\text{-}C_7H_{16}\}$ agreement with Lundberg's results(24)

TABLE 1

Excess molar enthalpies H^E for (methylcylopentane + another liquid) and (methylcyclohexane + another liquid) at 298.15 K and atmospheric pressure

x_1	$H^E/J.mol^{-1}$	x_1	$H^E/J.mol^{-1}$	x_1	$H^E/J.mol^{-1}$	x_1	$H^E/J.mol^{-1}$
$\{x_1 c\text{-}C_5H_9CH_3 + x_2 c\text{-}C_5H_{10}\}$							
0.0446	- 1.47	0.3159	-10.63	0.5699	-12.08	0.9322	-2.74
0.1561	- 6.01	0.4000	-11.93	0.6621	-10.94		
0.2332	- 8.62	0.4840	-12.37	0.8137	-7.22		
$\{x_1 c\text{-}C_5H_9CH_3 + x_2 c\text{-}C_6H_{11}CH_3\}$							
0.0595	-10.03	0.3849	-49.31	0.6423	-47.24	0.9491	-9.74
0.2009	-32.37	0.4746	-52.04	0.7264	-40.51		
0.2918	-42.66	0.5597	-51.30	0.8554	-24.90		
$\{x_1 c\text{-}C_6H_{11}CH_3 + x_2 n\text{-}C_7H_{16}\}$							
0.0622	7.68	0.3575	31.14	0.6133	35.98	0.8550	21.41
0.1689	17.65	0.4437	34.97	0.6945	33.34	0.9042	15.98
0.2609	25.53	0.5285	36.43	0.7802	28.49		
$\{x_1 c\text{-}C_6H_{11}CH_3 + x_2 n\text{-}C_{10}H_{22}\}$							
0.0810	20.39	0.4250	75.16	0.6782	76.14	0.8867	40.59
0.2126	47.30	0.5144	80.18	0.7513	68.09	0.9262	29.86
0.3192	64.58	0.5983	80.33	0.8250	56.09		
$\{x_1 c\text{-}C_6H_{11}CH_3 + x_2 c\text{-}C_5H_{10}\}$							
0.0395	-12.8	0.2893	-92.0	0.5388	-112.3	0.9238	-32.6
0.1402	-49.9	0.3702	-104.6	0.6333	-105.9		
0.2114	-71.6	0.4526	-111.2	0.7938	-75.7		

TABLE 1 - continued

x_1	H^E/J.mol^{-1}	x_1	H^E/J.mol^{-1}	x_1	H^E/J.mol^{-1}	x_1	H^E/J.mol^{-1}
$\{x_1c\text{-}C_6H_{11}CH_3 + x_2C_6H_6\}$							
0.0782	270.5	0.2604	665.2	0.5009	788.9	0.7975	433.8
0.1195	379.4	0.3354	748.6	0.5899	735.4	0.9234	150.6
0.1841	535.0	0.4166	790.0	0.6940	618.8		
$\{x_1c\text{-}C_6H_{11}CH_3 + x_2CCl_4\}$							
0.0843	48.2	0.2766	134.2	0.5215	156.2	0.8105	83.2
0.1285	73.9	0.3540	151.5	0.6097	143.8	0.9291	28.9
0.1968	108.1	0.4368	159.7	0.7112	120.2		

TABLE 2

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

Mixture	A_0	A_1	A_2	A_3	s
$x_1c\text{-}C_5H_9CH_3$					
$+ x_2c\text{-}C_5H_{10}$	-49.86	-0.10	8.16	-	0.17
$+ x_2c\text{-}C_6H_{11}CH_3$	-208.74	6.62	20.49	-21.95	0.16
$x_1c\text{-}C_6H_{11}CH_3$					
$+ x_2n\text{-}C_7H_{16}$	143.96	32.21	13.79	-	0.30
$+ x_2n\text{-}C_{10}H_{22}$	317.94	69.27	38.72	31.43	0.48
$+ x_2c\text{-}C_5H_{10}$	-453.9	-25.4	28.6	-	1.4
$+ x_2C_6H_6$	3169.8	-556.1	-237.1	-476.2	5.6
$+ x_2CCl_4$	637.7	-107.9	-94.8	-	2.0

$$H^E/J.mol^{-1} = x_1x_2[136.3 + 27.7(x_1 - x_2)] \quad (3)$$

is excellent, while those of Vesely et al.(22) are considerably lower and those of Alessi et al.(23) are much higher than our values. Holzhauer and Ziegler(21) report enthalpy data at one composition only, that is at $x_1 = 0.5109$ and 298.15 K $H^E = 34.2$ J.mol^{-1}, in excellent accord with our results. Similarly, upon interpolation Brandt's excess enthalpies(25) are very close to those determined by us. For $\{x_1C_6H_{11}CH_3 + x_2c\text{-}C_5H_{10}\}$ only H^E at equimolar composition has been measured previously: de St.Romain et al.(26) found $H^E(x_1=0.5) = - 112$ J.mol^{-1}, in excellent agreement with our -113.5 J.mol^{-1}. Data on H^E of $\{x_1C_6H_{11}CH_3 + x_2C_6H_6\}$, obtained with Van Ness type isothermal displacement calorimeters, have been reported by Nagata et al.(27) as well as by Tanaka et al.(28). Both sets agree satisfactorily with our results. Finally, H^E of $\{x_1C_6H_{11}CH_3 + x_2CCl_4\}$ has been measured with a flow calorimeter by Harsted and Thomsen.(29) Their values are very close to ours, i.e. at $x_1 = 0.5$ they report 162.8 J.mol^{-1} as compared to 159.4 J.mol^{-1} from our experiments.

A detailed discussion of our results in terms of the KGB group contribution theory(30) is in preparation.

ACKNOWLEDGMENTS

Financial support received within the frame of the Austrian-French program on scientific and technical cooperation is gratefully acknowledged by E.W. and J.-P.E.G.

REFERENCES

1. A.Inglese, E.Wilhelm, J.-P.E.Grolier and H.V.Kehiaian, J.Chem. Thermodyn., 12 (1980) 217.
2. A.Inglese, E.Wilhelm, J.-P.E.Grolier and H.V.Kehiaian, J.Chem. Thermodyn., 12 (1980) 1047.
3. A.Inglese, E.Wilhelm, J.-P.E.Grolier and H.V.Kehiaian, J.Chem. Thermodyn., 13 (1981) 229.
4. E.Wilhelm, A.Inglese, J.-P.E.Grolier and H.V.Kehiaian, J.Chem. Thermodyn., 14 (1982) 33.

5. E.Wilhelm, A.Inglese, J.-P.E.Grolier and H.V.Kehiaian, J.Chem. Thermodyn., 14 (1982) 517.
6. J.-P.Grolier, A.Inglese and E.Wilhelm, J.Chem.Eng.Data, 27 (1982) 333.
7. A.Inglese, J.-P.E.Grolier and E.Wilhelm, J.Chem.Eng.Data, 28 (1983) 124.
8. J.-P.E.Grolier, A.Inglese and E.Wilhelm, J.Chem.Thermodyn., 16 (1984)67.
9. A.Inglese, J.-P.E.Grolier and E.Wilhelm, Fluid Phase Equil., 15 (1984) 287.
10. E.Wilhelm, A.Inglese and J.-P.E.Grolier, J.Chem.Eng.Data, 28 (1983) 202.
11. A.Lainez, M.M.Rodrigo, E.Wilhelm and J.-P.E.Grolier, J.Chem.Eng.Data, 34 (1989) 332.
12. M.A.Siddiqi, G.Götze and F.Kohler, Ber.Bunsenges.Phys.Chem., 84 (1980) 529.
13. M.A.Siddiqi and F.Kohler, Ber.Bunsenges.Phys.Chem., 85 (1981) 17.
14. M.A.Siddiqi, J.Chem.Thermodyn., 13 (1981) 1151.
15. M.A.Siddiqi, P.Svejda and F.Kohler, Ber.Bunsenges.Phys.Chem., 87 (1983) 1176.
16. J.-P.E.Grolier, G.C.Benson and P.Picker, J.Chem.Thermodyn., 7 (1975) 89.
17. E.Wilhelm, Ber.Bunsenges.Phys.Chem., 81 (1977) 1150.
18. E.Wilhelm, A.Inglese, A.H.Roux and J.-P.E.Grolier, Fluid Phase Equil., 34 (1987) 49.
19. R.H.Stokes, K.N.Marsh and R.P.Tomlins, J.Chem.Thermodyn., 1 (1969) 211.
20. IUPAC, Pure Appl.Chem., 58 (1986) 1677.
21. J.K.Holzhauer and W.T.Ziegler, J.Phys.Chem., 79 (1975) 590.
22. F.Vesely, A.V.Mikulic, V.Svoboda and J.Pick, Collect.Chem.Commun., 40 (1975) 2551.
23. P.Alessi, I.Kikic and V.Longo: see *Handbook of Heats of Mixing*, by J.J.Christensen, R.W.Hanks and R.M.Izatt, Wiley, New York, 1982, p.531.
24. S.W.Lundberg, J.Chem.Eng.Data, 9 (1964) 193. See also Int.DATA Ser., Sel.Data Mixtures, Ser.A, (1974) 219.
25. H.Brandt, Z.Phys.Chem. (Neue Folge), 2 (1954) 104.
26. P.de St.Romain, H.T.Van and D.Patterson, J.Chem.Soc., Faraday Trans.1, 75 (1979) 1700.
27. I.Nagata, H.Asano and K.Fujiwara, Fluid Phase Equil., 1 (1978) 211.
28. K.Tamura, S.Murakami and R.Fujishiro, J.Chem.Thermodyn., 13 (1981) 47.
29. B.S.Harsted and E.S.Thomsen, J.Chem.Thermodyn., 7 (1975) 369.
30. H.V.Kehiaian, J.-P.E.Grolier and G.C.Benson, J.Chim.Phys., 75 (1978) 1031.