ELSEVIER

Thermochimica Acta 292 (1997) 39–44

thermochimica acta

Excess properties of N,N,N',N'-tetramethylalkanediamine + n-heptane: A study of the N-N proximity effect

Abdallah Dahmani[a,*], Ahmed Ait Kaci[a], Jacques Jose[b]

[a] *Laboratoire de thermodynamique des mélanges organiques, Institut de chimie, USTHB, BP.32 El-Alia, 16111 Bab-Ezzouar, Alger, Algeria*
[b] *Laboratoire de chimie analytique I, Université Claude Bernard (Lyon I), 43, bd du 11 Novembre 1918, 69622 Villeurbanne, France*

Received 3 July 1996; received in revised form 11 October 1996; accepted 15 November 1996

Abstract

The vapour pressure of liquid n-heptane + N,N,N',N' - tetramethylalkanediamine, $(CH_3)_2$ N-$(CH_2)_u$–$N(CH_3)_2$ ($u = 1,2$), mixtures were measured by a static method in the 303.15–343.15 K range at 10 K intervals. The excess molar enthalpies were also measured at 303.15 K.

The molar excess Gibbs energies, calculated from the vapour–liquid equilibrium data and the molar excess enthalpies compare satisfactorily with group contribution (DISQUAC) predictions.

The proximity effect of N-atoms produces a regular decrease of the interaction parameters.

Keywords: Diamines; Enthalpy; Excess functions; Vapour–liquid equilibria

1. Introduction

Diamines+n-alkanes represent one of the classes of organic mixtures which has been investigated with a view to testing group contribution models and to analyze the intramolecular effect, especially the proximity effect.

As far as we know, only a few measurements on these mixtures are reported in literature [1,2]. Molar excess enthalpies, H^E of this class of compounds with n-alkanes are reported at 298.15 K [1]. Excess Gibbs energies, G^E were also measured by the head-gas chromatography technique at the same temperature and have been successfully interpreted in terms of the zero-approximation quasi-lattice group contribution theory [2], confirming the occurrence of the proximity effect.

Following our systematic study of the thermodynamic properties of mixtures containing organic molecules [3], we present in this paper complete data for vapour pressures of N,N,N',N'-tetramethyldiaminomethane (TMDM) and N,N,N',N'-tetramethylethylenediamine (TMED) with n-heptane at five temperatures between 303.15 and 343.15 K, and H^E at 303.15 K.

The purpose of this paper is to study the excess properties of these mixtures in terms of DISQUAC, an extended quasi-chemical group contribution model [4], and to examine the proximity effect of N-atoms.

2. Experimental

n-Heptane (Prolabo, purity >99 mol%) was purified by fractional distillation. The vapour pressure, as determined, agrees with literature values [5]. The

---

*Corresponding author. Fax: 00 213 2 51 52 17.

0040-6031/97/$17.00
PII S0040-6031(96)03128-0

diamines (purity >99 mol%) were Janssen Chimica products, and were used without further purification.

The total vapour pressure measurements were obtained by a static method. Experimental details and procedure have been described elsewhere [6,7].

Excess molar enthalpies were measured at 303.15 K with a C 80 calorimeter (Setaram, France), a Calvet type microcalorimeter, with no vapour space. Mercury is used to separate the two cells containing the liquids under study. The performance of the apparatus was checked by determining H^E of n-hexane+cyclohexane at 298.15 K. Our results differ by <1% from those reported by Marsh [8].

3. Results

Table 1 shows the molar volume of the pure compounds, together with the experimental vapour pressures. The virial coefficients of diamines were evaluated from the Pitzer correlation [9]. The mixed virial coefficients were obtained from the Berthelot equation.

Vapour pressure measurements for the two mixtures at different temperatures are given in Table 2 together with the activity coefficients γ_1 and γ_2 and the values of the excess molar Gibbs energies G^E calculated by Barker's method [10] on the assumption that,

$$G^E/RT = x_1(1-x_1)\sum_{i=1}^{n} A_i(2x_1-1)^i \qquad (1)$$

The Wilson equation, namely,

$$G^E/RT = -x_1\ln[x_1+\Lambda_{12}(1-x_1)] - (1-x_1)\ln[(1-x_1)+\Lambda_{21}x_1] \qquad (2)$$

where x_1 is the mole fraction of the diamine, was also used.

The values of the parameters A_i and the standard deviation for the pressure are given in Table 3.

Table 4 gives the Wilson parameters. The two-parameter Wilson equation fits the pressure as good as Eq. (1).

Experimental molar excess enthalpies H^E at 303.15 K are reproduced in Table 5. The results have been fitted to the smoothing equation:

$$H^E_{\mathrm{exp}} = x_1(1-x_1)\sum_{i=1}^{n} a_i(2x_1-1)^i \qquad (3)$$

The values of the coefficients a_i and the standard deviations $\sigma(H^E)$ are given by,

$$\sigma(H^E) = \left[\sum_{i=1}^{n}(H^E - H^E_{\mathrm{exp}})^2/(N-n)\right]^{1/2} \qquad (4)$$

where N is the number of experimental points and n the number of coefficients a_i, were determined by the least-squares analysis and are reported in Table 6. By fitting $G^E(x_1=0.5)/T$ data with a second-degree polynomial in $1/T$, the derivative at 303.15 K gives $H^E = 436$ and 518 for TMDM + nC$_7$ and TMED + nC$_7$, respectively. These may be compared with the calorimetrically measured values of 500 and 465 J mol^{-1}. The agreement is reasonable since the quantitative evaluation of H^E from vapour pressure involves considerable uncertainty [11].

4. Theory

Diamines are regarded as possessing two types of surfaces: type a, alkane (CH_3 or CH_2 group) and type

Table 1

Molar volume V^*, vapour pressures p^*, and virial coefficients for the ij pair B_{ij} and of the pure compounds (i = j)

T/K	n-heptane			TMDM				TMED			
	V^*/ (cm^3 mol^{-1})	p^*/ (kPa)	B_{11}/ (cm^3 mol^{-1})	V^*/ (cm^3 mol^{-1})	p^*/ (kPa)	B_{11}/ (cm^3 mol^{-1})	B_{12}/ (cm^3 mol^{-1})	V^*/ (cm^3 mol^{-1})	p^*/ (kPa)	B_{11}/ (cm^3 mol^{-1})	B_{12}/ (cm^3 mol^{-1})
303.15	146.93	7.786	−2699	127.29	14.557	−2092	−2377	149.56	2.781	−3495	−3062
313.15	148.86	12.324	−2443	129.06	22.297	−1907	−2156	151.34	4.702	−3134	−2760
323.15	150.87	18.854	−2228	130.91	33.013	−1740	−1969	153.19	7.672	−2833	−2507
333.15	152.98	27.984	−2043	132.85	47.431	−1600	−1809	155.11	11.981	−2580	−2291
343.15	155.20	40.428	−1883	134.90	66.349	−1478	−1669	157.13	18.101	−2363	−2106

Table 2
Values of the vapour pressure p, deviations $\Delta p = 100(p - p_{\mathrm{cal}})/p$, activity coefficients γ_1 and γ_2 and excess molar Gibbs energies G^E

TMDM (1)+*n*-heptane (2)						TMED (1)+*n*-heptane (2)					
x_1	p/kPa	Δp	γ_1	γ_2	G^E/(J mol^{-1})	x_1	p/kPa	Δp	γ_1	γ_2	G^E/(J mol^{-1})
303.15 K											
0.0702	8.587	0.42	1.2369	1.0011	40	0.1316	7.2624	−0.45	1.1998	1.0044	70
0.1557	9.388	0.36	1.1954	1.0054	82	0.2449	6.7903	0.64	1.1458	1.0152	113
0.2372	10.060	0.07	1.1597	1.0129	113	0.3826	6.1855	0.65	1.0939	1.0369	143
0.3508	10.856	−0.68	1.1161	1.0293	144	0.5145	6.5194	−0.37	1.0563	1.0668	150
0.4693	11.699	−0.40	1.0780	1.0544	160	0.6584	4.7794	−1.03	1.0270	1.1100	134
0.5749	12.418	0.12	1.0504	1.0848	159	0.7736	4.1994	−0.15	1.0116	1.1531	104
0.6791	12.942	−0.41	1.0290	1.1230	143	0.8643	3.7045	0.90	1.0041	1.1927	69
0.7655	13.574	0.88	1.0156	1.1619	119						
0.8744	14.036	0.33	1.0046	1.2216	73						
0.8824	14.104	0.54	1.0040	1.2265	70						
313.15 K											
0.0702	13.486	0.63	1.1944	1.0007	34	0.1316	11.530	0.47	1.1790	1.0044	66
0.1557	14.584	0.24	1.1655	1.0039	71	0.2449	10.799	0.58	1.1280	1.0147	106
0.2372	15.569	0.02	1.1390	1.0096	100	0.3826	9.869	0.59	1.0801	1.0350	132
0.3508	16.760	−0.63	1.1047	1.0226	129	0.5145	8.841	−0.39	1.0467	1.0617	137
0.4693	18.034	−0.31	1.0727	1.0437	145	0.6584	7.702	−0.99	1.0217	1.0985	121
0.5749	19.088	0.04	1.0482	1.0704	146	0.7736	6.821	−0.06	1.0091	1.1334	93
0.6791	19.876	−0.48	1.0284	1.1056	133	0.8643	6.069	0.83	1.0032	1.1641	61
0.7655	20.840	0.86	1.0156	1.1422	112						
0.8744	21.557	0.45	1.0046	1.2003	70						
0.8824	21.623	0.53	1.0041	1.2051	67						
323.15 K											
0.0702	20.488	0.76	1.1624	1.0004	30	0.1316	17.686	0.44	1.1556	1.0044	61
0.1557	21.966	0.19	1.1436	1.0026	70	0.2449	16.595	0.49	1.1066	1.0145	96
0.2372	23.366	0.01	1.1246	1.0067	89	0.3826	15.213	0.52	1.0630	1.0332	117
0.3508	25.079	−0.58	1.0974	1.0171	117	0.5145	13.682	−0.38	1.0345	1.0562	118
0.4693	26.918	−0.29	1.0700	1.0353	135	0.6584	11.987	−0.92	1.0148	1.0851	101
0.5749	28.421	−0.03	1.0477	1.0595	138	0.7736	10.698	0.05	1.0057	1.1097	75
0.6791	29.571	−0.49	1.0287	1.0926	128	0.8643	9.591	0.71	1.0018	1.1292	49
0.7655	30.924	0.69	1.0160	1.1286	109						
0.8744	32.042	0.61	1.0049	1.1873	70						
0.8824	32.151	0.70	1.0043	1.1922	66						
333.15 K											
0.0702	30.216	0.74	1.1463	1.0004	28	0.1316	26.309	0.43	1.1415	1.0042	59
0.1557	32.180	0.08	1.1305	1.0022	58	0.2449	24.730	0.44	1.0954	1.0138	91
0.2372	34.113	−0.02	1.1140	1.0058	83	0.3826	22.738	0.48	1.0551	1.0312	109
0.3508	36.493	−0.50	1.0899	1.0151	111	0.5145	20.532	−0.36	1.0293	1.0520	109
0.4693	39.037	−0.21	1.0651	1.0316	128	0.6584	18.085	−0.90	1.0120	1.0773	92
0.5749	41.128	0.06	1.0446	1.0538	131	0.7736	16.256	0.10	1.0045	1.0977	68
0.6791	42.768	−0.28	1.0270	1.0845	122	0.8643	14.676	0.67	1.0014	1.1130	44
0.7655	44.523	0.59	1.0151	1.1179	104						
0.8744	46.001	0.37	1.0046	1.1725	67						
0.8824	46.043	0.23	1.0040	1.1772	63						
343.15 K											
0.0702	43.393	0.73	1.1328	1.0002	26	0.1316	38.075	0.40	1.1291	1.0040	55
0.1557	45.980	0.08	1.1212	1.0016	55	0.2449	35.851	0.39	1.0867	1.0128	86

Table 2
(Continued)

TMDM (1)+*n*-heptane (2)						TMED (1)+*n*-heptane (2)					
x_1	p/kPa	Δp	γ_1	γ_2	G^E/(J mol^{-1})	x_1	p/kPa	Δp	γ_1	γ_2	G^E/(J mol^{-1})
0.2372	48.578	0.01	1.1078	1.0046	79	0.3826	33.058	0.45	1.0498	1.0288	103
0.3508	51.783	−0.45	1.0868	1.0127	107	0.5145	29.971	−0.33	1.0262	1.0479	103
0.4693	55.170	−0.26	1.0640	1.0279	125	0.6584	26.536	−0.89	1.0106	1.0706	86
0.5749	58.018	0.04	1.0444	1.0491	130	0.7736	24.011	0.14	1.0039	1.0887	63
0.6791	60.301	−0.15	1.0271	1.0790	122	0.8643	21.817	0.63	1.0012	1.1019	40
0.7655	62.403	0.30	1.0153	1.1121	104						
0.8744	64.533	0.38	1.0047	1.1671	67						
0.8824	64.706	0.43	1.0041	1.1718	64						

Table 3
Coefficients A_i and standard deviations of pressure σ/(Pa) for the least-squares representation by Eq. (1)

T/(K)	TMDM (1)+*n*-heptane (2)			TMED (1)+*n*-heptane (2)		
	A_1	A_2	σ/(Pa)	A_1	A_2	σ/(Pa)
303.15	0.2553	−0.0130	0.0053	0.2386	−0.0060	0.0078
313.15	0.2251	−0.0273	0.0054	0.2108	−0.0162	0.0074
323.15	0.2038	−0.0414	0.0057	0.1769	−0.0313	0.0066
333.15	0.1876	−0.0413	0.0042	0.1590	−0.0345	0.0063
343.15	0.1784	−0.0475	0.0039	0.1451	−0.0334	0.0060

Table 4
Coefficients Λ_{ij} standard deviations of pressure σ/(Pa) for least-squares representation by the Wilson equation Eq. (2)

T/(K)	TMDM (1)+*n*-heptane (2)			TMED (1)+*n*-heptane (2)		
	Λ_{12}	Λ_{21}	σ/(Pa)	Λ_{12}	Λ_{21}	σ/(Pa)
303.15	0.2312	0.0092	0.0052	0.0526	0.1768	0.0077
313.15	0.3499	−0.1672	0.0053	−0.0931	0.2798	0.0072
323.15	0.4586	−0.3464	0.0053	−0.3235	0.4231	0.0062
333.15	0.4537	−0.3577	0.0039	−0.4011	0.4602	0.0058
343.15	0.4942	−0.4331	0.0034	−0.4265	0.4656	0.0056

Table 5
Experimental molar excess enthalpies H^E at 303.15 K

TMDM (1)+*n*-heptane (2)				TMED (1)+*n*-heptane (2)			
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})
0.1124	200	0.6443	462	0.0493	105	0.3972	466
0.1989	332	0.7396	375	0.0812	155	0.5256	465
0.2703	407	0.7844	334	0.1162	213	0.6247	434
0.3786	471	0.8547	250	0.1724	301	0.7217	364
0.4007	480			0.2183	345	0.7844	290
0.4836	498			0.2504	375	0.8291	238
0.6053	478			0.3008	416	0.9157	134

Table 6
Coefficients a_j and standard deviations σ/H^E for least-squares representation by Eq. (2) of H^E at 303.15 K

Mixtures	a_1	a_2	σ/(J mol^{-1})
TMDM (1)+*n*-heptane (2)	2006.009	−297.623	4
TMED (1)+*n*-heptane (2)	1891.621	−252.602	4

n, nitrogen (N group). The geometrical parameters have been calculated as before [1]. The solvent, *n*-heptane (surface type *a*) is regarded as a homogeneous molecule with a previously estimated surface [1]. The two types of surfaces, *a* and *n*, generate a single pair of contact (*a*,*n*). The equations used to calculate G^E and H^E are the same as in other publications [12,13].The temperature dependence of the interaction parameters has been expressed in terms of dispersive (dis) and/or quasi-chemical (quac) interchange coefficients:

$$C_{\mathrm{an,l}}(\mathrm{dis\,or\,quac}),\ \mathrm{where\,l} = 1(\mathrm{Gibbs\,energy})\ \mathrm{or}\ \mathrm{l} = 2(\mathrm{enthalpy}).$$

5. Comparison with experiment and discussion

The thermodynamic properties of diamines+*n*-alkanes have been investigated previously [1,2]. These systems are characterized by a single contact (*a*, *n*). The random-mixing approximation describes the shapes of H^E and G^E curves very well.

A more careful examination shows, however, that the experimental G^E and H^E data have maxima slightly shifted from those calculated by the model in the random-mixing approximation, indicating the presence of weak orientational contributions. For this reason, we decided to examine the mixtures investigated in this work with the DISQUAC model. We

Table 7
Interchange energy coefficients, dispersive $C^{dis}_{st,l}$ and quasichemical $C^{quac}_{st,l}$ ($z = 4$), for contact (*a*, *n*), CH_2 or CH_3 (type *a*), N (type *n*)

contact (*s*, *t*)		$C^{dis}_{st,1}$	$C^{dis}_{st,2}$	$C^{quac}_{st,1}$	$C^{quac}_{st,2}$
(*a*, *n*)	TMDM (1)+*n*-C_7 (2)	30	75	3.33	11.1
	TMED (1)+*n*-C_7 (2)	30	75	4.5	12.1
	Trimethylamine+*n*-C_6	30	75	6.2	15.65

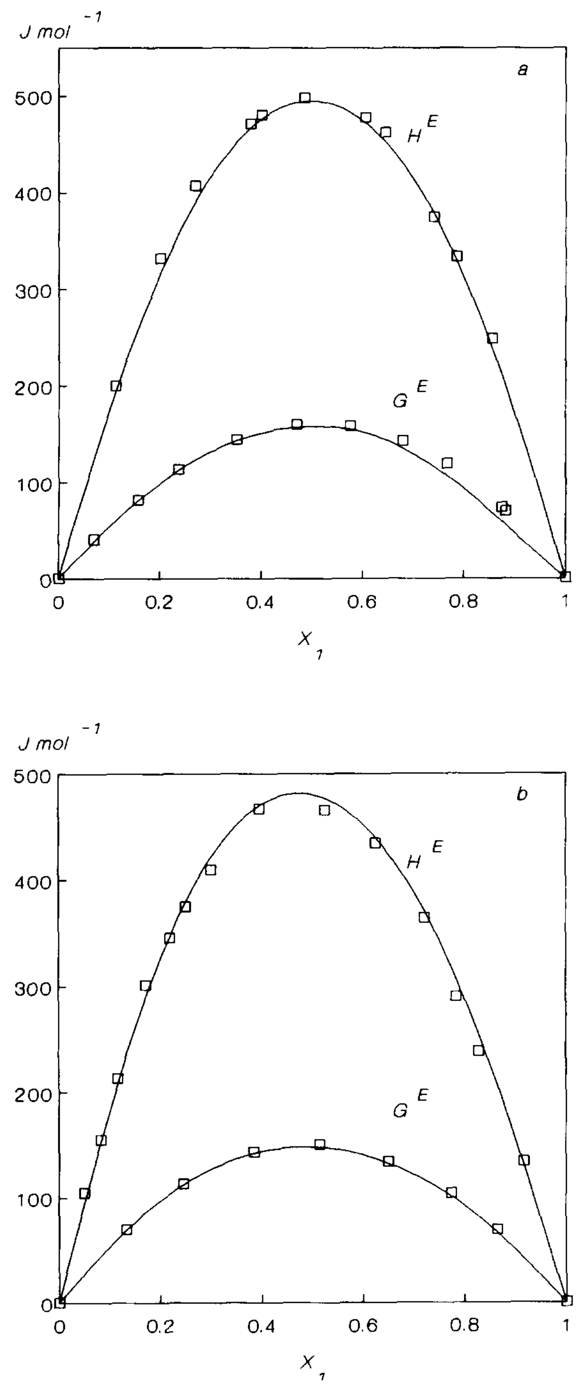

Fig. 1. Comparison of the theory with experiment for the molar excess Gibbs energy G^E and the molar enthalpy H^E at 303.15 K: (a) TMDM (1)+*n*-C_7 (2); and (b) TMED (1)+*n*-C_7 (2). Lines represents predicted values. Points represent experimental results.

reduced the dispersive coefficients $C^{dis}_{an,l}$ to $30(l = 1)$ and $75(l = 2)$ and adjusted the quasi-chemical coefficients to the values of trimethylamine+hexane reported in [14] and G^E and H^E to the excess properties of the diamine+n-heptane of the present work. It may be seen from Table 7 that the quasi-chemical parameters increase with the 'distance' u between the N-atoms and tend towards the limiting values of the monamine+n-alkane.

Fig. 1 shows the experimental and theoretical curves of G^E and H^E at 303.15 K. The DISQUAC model reproduces quite accurately the experimental measurements.

The most interesting result of our study is the confirmation of the proximity effect in linear diamines, quite similar to the effect observed in dichloroalkanes [15,16], acetals [17] and dibromoalkanes [18].

References

[1] I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H.V. Kehiaian, Fluid Phase Equilib., 11 (1983) 1.

[2] D. Cancellu, B. Marongiu and S. Porcedda, Thermochim. Acta, 178 (1991) 33.

[3] A. Dahmani, A.A. Kaci, I. Mokbel, G. Ghanem and J. Jose, J. Chim. Phys., 92 (1995) 1093.

[4] H.V. Kehiaian, Pure Appl. Chem., 57 (1985) 15.

[5] J.M. Riddick., Molecular thermodynamics of fluid phase equilib., Prentice-Hall, Englewood Cliffs, NJ (1969) pp. 523 .

[6] J. Jose, R. Philippe and P. Clechet, Bull. Soc. Chim., France., 8 (1971) 2860.

[7] M.A. Michou-Saucet, J. Jose, C. Michou-Saucet and J.C. Merlin, Thermochim. Acta., 75 (1984) 85.

[8] K.N. Marsh, Int. Data Ser., Sel. Data Mixtures, Ser. A., (1973) 22.

[9] K.S. Pitzer and R.F. Curl, J. Am. Chem. Soc., 79 (1957) 2369.

[10] J.A. Barker, Aust. J. Chem., 6 (1953) 207.

[11] J.S. Rowlinson, Liquids and Liquid mixtures, 3rd edn., Butterworth Scientific, London (1982) p. 138.

[12] H.V. Kehiaian and B. Marongiu, Fluid Phase Equilib., 40 (1988) 23.

[13] M.R. Tiné and H.V. Kehiaian, Fluid Phase Equilib., 32 (1987) 211.

[14] H. Wolff and R. Wurtz, Ber. Bunsenges. Phys. Chem., 72 (1968) 101.

[15] J.P.E. Grolier and H.V. Kehiaian, J. Chim. Phys., 70 (1973) 807.

[16] C. Polo, C,G. loza, M.R. Kechavararz and H.V. Kehiaian, Ber. Bunsenges. Phys. Chem., 84 (1980) 525.

[17] H.V. Kehiaian, M.R. Tiné, L. Lepori, E. Matteoli and B. Marongiu, Fluid Phase Equilib., 46 (1989) 131.

[18] M.J. Artal, J.M. Embid, I. Velasco, I. Velasco and H.V. Kehiaian, Fluid Phase Equilib., 70 (1991) 267.