J Therm Anal Calorim (2010) 101:1121–1125
DOI 10.1007/s10973-010-0732-x

Excess molar enthalpies of dichloropropane + *n*-alkane mixtures

Study on the effect of increasing the chain length of the *n*-alkane and the influence of the chlorine position

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Received: 31 July 2009 / Accepted: 18 February 2010 / Published online: 19 March 2010

Abstract We have determined the excess molar enthalpies H_m^E at 298.15 K and normal atmospheric pressure for the binary mixtures containing dichloropropane and *n*-alkane [{xCH$_2$ClCHClCH$_3$ + (1−x) C$_n$H$_{2n+2}$ (n = 6, 8, 10, 12)} and {xCH$_2$ClCH$_2$CH$_2$Cl + (1−x) C$_n$H$_{2n+2}$ (n = 8, 10)}] using a Calvet microcalorimeter. The H_m^E values for all the mixtures show endothermic behaviour for the whole composition range. The Redlich–Kister equation was used to correlated the experimental values. The experimental excess molar enthalpies were examined on basis of the DISQUAC group-contribution model and the UNIFAC group-contribution method using the version considered by Larsen et al. The experimental and calculated results are discussed in terms of molecular interactions and the proximity effect.

Keywords Alkane · Dichloropropane · DISQUAC · Excess molar enthalpies · UNIFAC

Introduction

We have determined the excess molar enthalpies of {CH$_2$ClCHClCH$_3$ + (1−x) C$_n$H$_{2n+2}$ (n = 6, 8, 10, 12)} and {xCH$_2$ClCH$_2$CH$_2$Cl + (1−x) C$_n$H$_{2n+2}$ (n = 8, 10)} mixtures at the temperature of 298.15 K and atmospheric pressure. Values of excess molar enthalpies over the entire range of composition were measured using a Calvet microcalorimeter. The results were adjusted by a variable-degree polynomial. The measured excess molar enthalpies of the systems mentioned above were used to test the predictions of DIQUAC [1] and UNIFAC (UNIquac Functional-Group Activity Coefficients) group-contribution model designated UNIFAC II (modified UNIFAC, in the version considered by Larsen et al. [2]). Several H_m^E data have been published in the literature for 1,3-dichloropropane + *n*-alkane [3–9] and only one H_m^E data source on mixtures containing the 1,2-dichloropropane + *n*-alkane [10] can be found in the literature. As far as we know, there exist no previous measurements on mixtures 1,3-dichloropropane + *n*-alkane (n = 8, 10) and 1,2-dichloropropane + *n*-alkane (n = 8, 10, 12).

Experimental

The sources and the purities of the chemicals substances employed were: CH$_2$ClCH$_2$CH$_2$Cl (Aldrich 0.99), CH$_2$ClCHClCH$_3$ (Fluka $>$ 0.99), C$_6$H$_{14}$ (Fluka $>$ 0.995), and C$_n$H$_{2n+2}$ (n = 8, 10, 12) (Aldrich $>$ 0.99). Before measurements, all liquids were subjected to no further purification other than drying with Union Carbide 0.4 nm molecular sieves.

The experimental excess molar enthalpies were determined using a Calvet microcalorimeter with a calorimeter-cell volume of approximately 10 cm^3 and equipped with a device allowing operation in the absence of vapour phase linked to a Philips PM2535 voltimeter and to a data acquisition system. The microcalorimeter was calibrated electrically using a stabilized current source (EJP-30, Setaram). The performance of the apparatus and procedures was checked by determining excess enthalpies for the

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standard system *n*-hexane + cyclohexane at 298.15 K and our results differ by less than 1% from those of McGlashan and Stoeckli [11]. Both the calibration and operation conditions are described by Paz Andrade et al. [12, 13]. The samples were prepared by mass using a Mettler H51 balance with a accuracy of $\pm 10^{-5}$ g covering the whole composition range of the mixtures, with an uncertainty in mole fraction estimated to be lower than $\pm 10^{-4}$. The precision of the excess molar enthalpies is estimated to better than 1%. All molar quantities are based on the IUPAC relative atomic mass table [14].

Results and discussion

Experimental values of H_m^E for the six mixtures $\{x\mathrm{CH_2ClCHClCH_3} + (1-x)\ \mathrm{C}_n\mathrm{H}_{2n+2}\ (n = 6, 8, 10, 12)\}$ and $\{x\mathrm{CH_2ClCH_2CH_2Cl} + (1-x)\ \mathrm{C}_n\mathrm{H}_{2n+2}\ (n = 8, 10)\}$ are listed in Table 1. The experimental results for each mixture were fitted with polynomials by least-squares of the form:

$$H_m^E/\left(\mathrm{J\,mol^{-1}}\right) = x(1-x)\sum_{i=1}^{n} A_i(2x-1)^{i-1} \qquad (1)$$

Equation 1 is a Redlich–Kister fitting polynomial [15] and the coefficients A_i were determined by an unweighted least-squares method using the Marquardt algorithm [16]. The degree of the polynomial used in Eq. 1 for each mixture has been determined applying an *F* test [17]. The parameters, A_i, and the standard deviations, $s\ (H_m^E)$, are summarized in Table 2 for each system. A graphical representation of the experimental values of H_m^E plotted against *x* together with the smoothing curves is shown, for

Table 1 Excess molar enthalpies at 298.15 K for binary mixtures: *x* dichloroalkane + (1−*x*) alkane

x	$H_m^E/\mathrm{J\,mol^{-1}}$	x	$H_m^E/\mathrm{J\,mol^{-1}}$	x	$H_m^E/\mathrm{J\,mol^{-1}}$	x	$H_m^E/\mathrm{J\,mol^{-1}}$	x	$H_m^E/\mathrm{J\,mol^{-1}}$	x	$H_m^E/\mathrm{J\,mol^{-1}}$
$x\mathrm{CH_2ClCHClCH_3} + (1-x)\ \mathrm{CH_3(CH_2)_4CH_3}$											
0.0589	242	0.2511	889	0.4081	1181	0.5626	1236	0.7175	1028	0.9231	351
0.0635	262	0.3040	1010	0.4706	1232	0.5876	1209	0.7522	940	0.9652	173
0.1277	489	0.3161	1056	0.4863	1240	0.6271	1169	0.8106	755		
0.1944	712	0.3653	1147	0.5165	1239	0.6579	1132	0.8613	584		
0.2205	785	0.3750	1159	0.5362	1237	0.6660	1127	0.8792	522		
$x\mathrm{CH_2ClCHClCH_3} + (1-x)\ \mathrm{CH_3(CH_2)_6CH_3}$											
0.0708	288	0.2981	1069	0.4797	1317	0.6824	1285	0.8341	875	0.9356	357
0.0837	343	0.3605	1185	0.5554	1351	0.7193	1222	0.8714	690	0.9660	197
0.1430	580	0.3999	1242	0.5632	1343	0.7610	1121	0.8960	568		
0.2157	842	0.4601	1299	0.6282	1320	0.8014	998	0.9051	523		
$x\mathrm{CH_2ClCHClCH_3} + (1-x)\ \mathrm{CH_3(CH_2)_8CH_3}$											
0.0757	348	0.2661	1008	0.4094	1288	0.6159	1403	0.7894	1126	0.9208	523
0.0912	403	0.2804	1035	0.4760	1362	0.6708	1370	0.8217	1013	0.9421	403
0.1050	465	0.3458	1183	0.5048	1387	0.7004	1329	0.8618	833	0.9729	201
0.1703	713	0.3970	1273	0.5600	1404	0.7530	1221	0.8831	732		
$x\mathrm{CH_2ClCHClCH_3} + (1-x)\ \mathrm{CH_3(CH_2)_{10}CH_3}$											
0.1027	459	0.3820	1327	0.5983	1518	0.7318	1353	0.8771	847	0.9699	258
0.1078	482	0.4478	1442	0.6329	1499	0.7693	1256	0.9052	684		
0.2103	867	0.5011	1497	0.6568	1465	0.8110	1128	0.9261	558		
0.2907	1113	0.5543	1520	0.6874	1428	0.8423	1007	0.9527	384		
$x\mathrm{CH_2ClCH_2CH_2Cl} + (1-x)\ \mathrm{CH_3(CH_2)_6CH_3}$											
0.0773	447	0.2458	1152	0.3607	1447	0.5285	1610	0.6764	1448	0.8010	1068
0.1082	600	0.2762	1236	0.4225	1547	0.5737	1589	0.7169	1351	0.8214	995
0.1558	817	0.2925	1292	0.4334	1559	0.6255	1542	0.7579	1226	0.8692	772
0.1903	953	0.3058	1328	0.4657	1587	0.6320	1536	0.7786	1151	0.9524	305
$x\mathrm{CH_2ClCH_2CH_2Cl} + (1-x)\ \mathrm{CH_3(CH_2)_8CH_3}$											
0.0932	535	0.2501	1216	0.4089	1610	0.5662	1681	0.7221	1441	0.9284	520
0.1298	718	0.3203	1432	0.4880	1685	0.6311	1631	0.7792	1263		
0.1762	932	0.3598	1518	0.4887	1687	0.6708	1561	0.8140	1116		
0.2078	1058	0.3991	1604	0.5110	1699	0.6801	1537	0.8590	911		

Table 2 Parameters A_i of Eq. 1 and standard deviations, s, for H_m^E

A_1	A_2	A_3	A_4	A_5	s
xCH$_2$ClCHClCH$_3$ + (1−x) CH$_3$(CH$_2$)$_4$CH$_3$					
4987	−304	−523	–	–	9
xCH$_2$ClCHClCH$_3$ + (1−x) CH$_3$(CH$_2$)$_6$CH$_3$					
5312	−1052	1841	–	−2826	7
xCH$_2$ClCHClCH$_3$ + (1−x) CH$_3$(CH$_2$)$_8$CH$_3$					
5530	−1419	1553	–	−1132	5
xCH$_2$ClCHClCH$_3$ + (1−x) CH$_3$(CH$_2$)$_{10}$CH$_3$					
5976	−1543	550	−531	406	4
xCH$_2$ClCH$_2$CH$_2$Cl + (1−x) CH$_3$(CH$_2$)$_6$CH$_3$					
6424	578	104	−383	–	4
xCH$_2$ClCH$_2$CH$_2$Cl + (1−x) CH$_3$(CH$_2$)$_8$CH$_3$					
6776	678	353	271	–	4

mixtures 1, 2-dichloropropane + n-alkane (n = 6, 8, 10, 12) and mixtures 1,3-dichloropropane + n-alkane (n = 8, 10), in Fig. 1.

The experimental excess molar enthalpies, H_m^E are positive for all the studied systems over the whole range of composition. This suggests the predominance of the breaking of previous interactions over the interactions established during the mixing process. The maximum values corresponding to those interactions oscillate between 1200 J mol^{-1} and 1700 J mol^{-1}, with the standard deviation varying between 4 J mol^{-1} for the system 1,3-dichloropropane + octane and 9 J mol^{-1} for 1,2-dichloropropane + hexane.

Baños et al. [10] measured H_m^E {xCH$_2$ClCHClCH$_3$ + (1−x) C$_n$H$_{2n+2}$ (n = 6, 16)} at 288.15, 298.15, 308.15, 308.15, 318.15 K and obtained for 1,2-dichloropropane + n-hexane $H_m^E(x = 0.5) = 1100$ J mol^{-1}, 12% lower than our, $H_m^E(x = 0.5) = 1251$ J mol^{-1}.

Baños et al. [7] measured H_m^E {xCH$_2$ClCH$_2$CH$_2$Cl + (1−x) C$_6$H$_{14}$}and {xCH$_2$ClCH$_2$CH$_2$Cl + (1−x) C$_{16}$H$_{34}$} at 288.15, 298.15, 308.15, 308.15, 318.15 K and their value $H_m^E(x = 0.5) = 1252$ J mol^{-1} for 1,3-dichloropropane + n-hexane at 298.15 K agrees satisfactorily with the value $H_m^E(x = 0.5) = 1254$ J mol^{-1} obtained by Polo et al. [8]. Ortega and Plácido [3–6] determined the H_m^E values for mixtures 1,3-dichloropropane + n-alkane (from C$_5$ to C$_{17}$) at 298.15 K and they obtained $H_m^E(x = 0.5) = 1564$ J mol^{-1} for 1,3-dichloropropane + n-heptane somewhat higher than $H_m^E(x = 0.5) = 1454$ J mol^{-1} reported by Grolier and Kehiaian [9].

The obtained curves are slightly asymmetric, with their maximum shifted around the rich compositions in dichloropropane. The maximum values of the excess molar enthalpies increase with the number of carbon atoms of the alkane, as can be seen in Fig. 3, which indicates that as the length of the alkane increases, the induced dipole–induced dipole interaction is stronger, thus raising the positive contribution to the excess molar enthalpy.

The different calorimetric behaviour of the mixtures CH$_2$ClCHClCH$_3$ + C$_n$H$_{2n+2}$ with CH$_2$ClCH$_2$CH$_2$Cl + C$_n$H$_{2n+2}$ is put down principally to smaller "proximity effect" in the latter, which means that when the –Cl groups get closer to each other, the dipole–dipole interactions of the dichloroalkane become weaker. This fact explains why the mixture containing 1,3-dichloropropane has a more endothermic behaviour than that containing 1,2-dichloropropane.

The group-contribution models UNIFAC (version Larsen et al.) and DISQUAC were applied to estimate excess molar enthalpies.

In order to compare the predictions of excess molar enthalpies for different group-contribution models, the percentage mean deviation, PMS, was used. It is defined by:

$$\mathrm{PMS} = (100/N)S\left(\left|H_{\exp} - H_{\mathrm{cal}}\right|/H_{\exp}\right) \qquad (2)$$

where $H_{\exp}$ and H_{cal} are the experimental and the predicted values for excess molar enthalpy and N the number of the experimental values for this property.

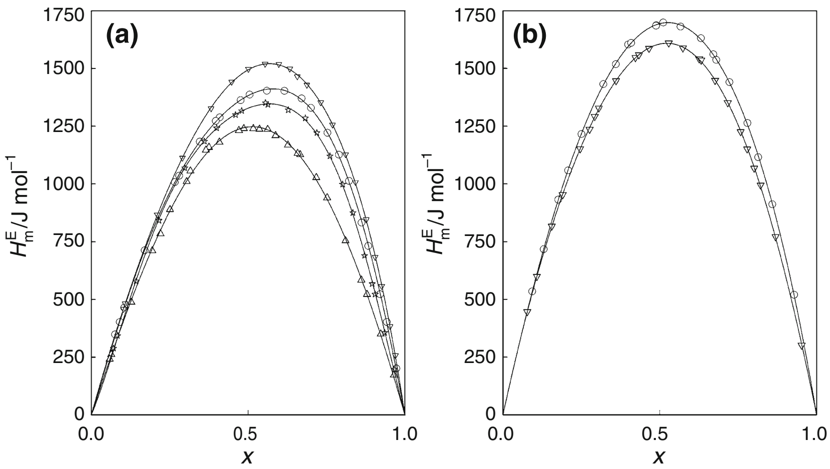

Fig. 1 Excess molar enthalpies H_m^E against mole fraction x at 298.15 K for: **a** xCH$_2$ClCHClCH$_3$ + (1−x) C$_n$H$_{2n+2}$. Experimental results: *upright triangle* hexane, *star* octane, *circle* decane, *inverted triangle* dodecane. **b** xCH$_2$ClCH$_2$CH$_2$Cl + (1−x) C$_n$H$_{2n+2}$: *inverted triangle* octane, *circle* decane, *solid line* fitting curves

Table 3 summarizes experimental values obtained in this work for equimolecular composition of excess molar enthalpies for our mixtures and the theoretical predictions using DISQUAC and UNIFAC II (version Larsen et al.) models. For comparison we have listed the PMS obtained with both group-contribution models. The results obtained by UNIFAC II are displayed in Fig. 2. Figure 3 illustrates the predictions obtained DISQUAC model. The maximum values of the experimental H_m^E, from available literature data sources and this work, are compared in Fig. 4, with those predicted by DISQUAC model and the UNIFAC II (Larsen's version) model.

Table 3 Comparison of experimental results with values calculated using theoretical models

System	PMS (UNIFAC II)/%	PMS (DISQUAC)/%
1,2-dichloropropane + hexane	8.2	9.2
1,2-dichloropropane + octane	8.2	10.4
1,2-dichloropropane + decane	7.4	13.0
1,2-dichloropropane + dodecane	5.7	13.3
1,3-dichloropropane + octane	2.9	3.8
1,3-dichloropropane + decane	5.7	1.4

The tested group-contribution models are in qualitative satisfactory agreement with the experimental excess molar enthalpy results, showing in every case average relative deviations lower than 13.3%. Figures 2 and 3 show that the shape of H_m^E vs. x curves are well predicted. In Fig. 4 we can see that the dependence of excess molar enthalpy, with the number of carbon atoms of the *n*-alkane is well predicted.

In general, the best results are achieved in UNIFAC II (version Larsen et al.). This may be due to the fact that Larsen et al. used a database [2] containing experimental values of H_m^E and V_m^E for the binary systems (1,2-dichloroethane + alkane or cyclohexane, 1-chlorobutane + alkane) for the determination of the interaction parameters between the CH_2 groups of the alkanes and the chlorine group. The choice of the database is very important for the goodness of predictions. In accordance with these, it is

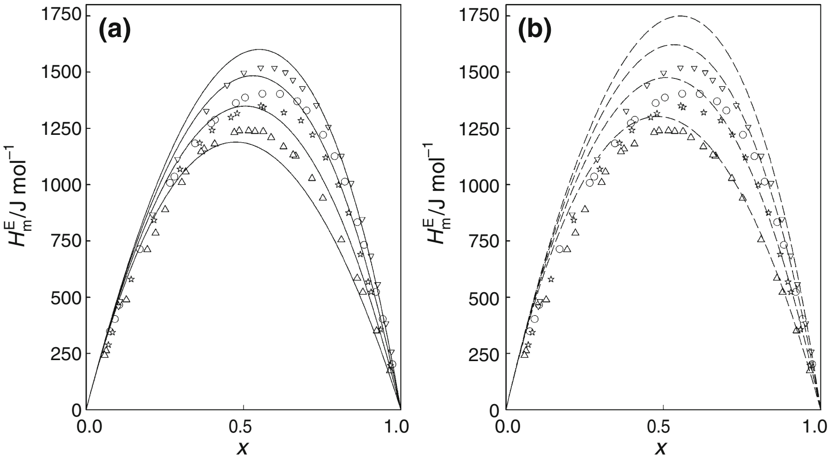

Fig. 2 Excess molar enthalpies H_m^E against mole fraction x at 298.15 K for $x CH_2ClCHClCH_3 + (1-x) C_nH_{2n+2}$, compared with the predictions of **a** UNIFAC II (*solid line*) and **b** DISQUAC (*dashed line*). Experimental results: *upright triangle* hexane, *star* octane, *circle* decane, *inverted triangle* dodecane

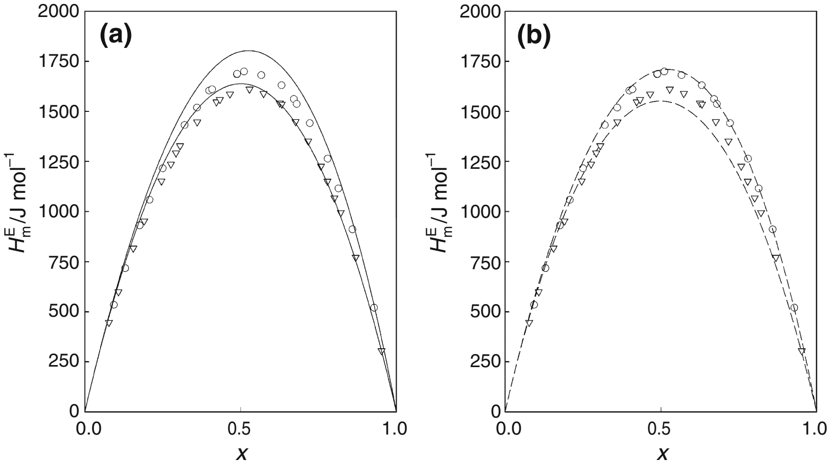

Fig. 3 Excess molar enthalpies H_m^E against mole fraction x at 298.15 K for $\{x CH_2ClCH_2CH_2Cl + (1-x) C_nH_{2n+2}\}$, compared with the predictions of **a** UNIFAC II (*solid line*) and **b** DISQUAC (*dashed line*). Experimental results: *inverted triangle* octane, *circle* decane

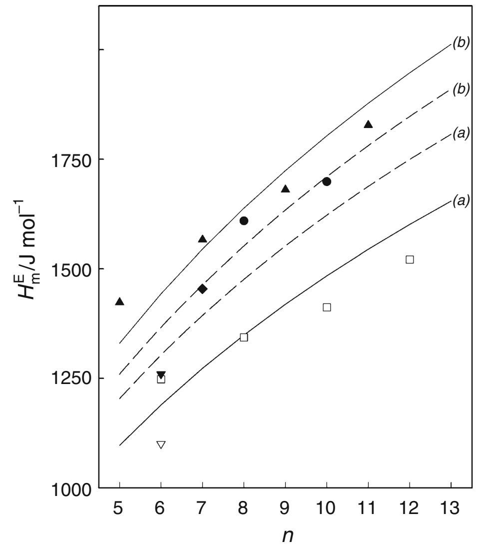

Fig. 4 Maximum values of excess molar volumes depending on the length of the alkane carbon chain. Experimental data: 1,2-dichloropropane + *n*-alkane (*open inverted triangle* Baños et al. (1989) [10]; *open square* present work); 1,3-dichloropropane + *n*-alkane (*filled upright triangle* Ortega and Plácido (1993) [3–6]; *filled inverted triangle* Baños et al. (1990) [7]; Polo et al. (1990); *filled diamond* Grolier and Kehiaian (1973); *filled circle* This work); Theoretical predictions: (*a*) 1,2-dichloropropane + *n*-alkane (*b*) 1,3-dichloropropane + *n*-alkane (UNIFAC II (*solid line*), DISQUAC (*dashed line*))

expected to find good results for the excess enthalpies of our mixtures because the molecules 1,2-dichloropropane and 1,2-dichloroethane are similar. Both molecules are α,β-dichloroalkanes and dichloroalkanes of short chain.

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