

# Calorimetric study of nitro group/solvent interactions

## Comparison with DISQUAC predictions

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**Abstract** A flow microcalorimeter, model 2277-LKB, has been used to determine excess enthalpies,  $H^E$ , at 298.15 K, for liquid mixtures containing 1-nitrobutane or 1-nitropentane or 1-nitrohexane + benzene or + tetrachloromethane. The experimental results, taken from literature, concerning thermodynamic properties of nitroalkanes + benzene or + tetrachloromethane mixtures have been interpreted in terms of the DISQUAC group contribution model. Two sets of structure-dependent interaction parameters for the nitro group/benzene and for the nitro group/tetrachloromethane contacts have been obtained. The model provides a fairly consistent description of the excess functions,  $G^E$  and  $H^E$  and of activity coefficients at infinite dilution,  $\gamma_i^\infty$ .

**Keywords** Benzene · DISQUAC model ·  
Experimental excess enthalpies · Nitroalkanes ·  
Tetrachloromethane

### Introduction

DISQUAC [1, 2] is a group contribution model based on the rigid lattice theory developed by Guggenheim [3] for liquid mixtures. This model calculates the excess thermodynamics properties as a sum of two contribution: one DIS, due to dispersive forces, always present, whatever the kind of molecules, and another QUAC, depending on specific chemical interactions. The quasichemical term is zero for mixtures of non-polar compounds, but also for mixtures

containing two polar constituents. In the last case similar kind and strength of interactions exerted by the two constituents allows that a mixture maintains the same structure of the pure liquid.

Following a coherent strategy, in the application of DISQUAC, we examined firstly mixtures of organic compounds of different polarity as alkanones [4], oxaalkanes [5, 6] and chloroalkylbenzenes [7] with linear and cyclic alkanes. Then, were considered mixtures containing the same classes above mentioned with solvents having a higher polarizability as benzene (B) and tetrachloromethane (T) [8–10].

Nitroalkanes are an important class of organic compounds used as solvent for cellulose acetate, vinyl resins, synthetic rubbers, fats, oils and dyes and as intermediate in organic synthesis [11]. These compounds are characterized by a relevant polarity; dipolar moments of nitro-compounds in *n*-hexane at 293 K are 3.56, 3.60 and 3.59 D for nitromethane, nitroethane and 1-nitropropane [12], respectively.

As a continuation of an investigation on nitroalkanes mixtures [13] in this paper we intend to present  $H^E$  experimental data on mixtures containing 1-nitrobutane or 1-nitropentane or 1-nitrohexane + benzene or + tetrachloromethane. The second purpose of this work is to interpret experimental data concerning thermodynamic properties as excess Gibbs energies,  $G^E$ , excess enthalpies,  $H^E$  and of activity coefficients at infinite dilution,  $\gamma_i^\infty$ , of nitroalkanes + benzene or + tetrachloromethane.

We expected that DISQUAC would permit the finding of parameters of the contact nitro group/benzene and nitro group/tetrachloromethane which vary regularly with the molecular structure of the polar compound. The input data are the molar excess Gibbs energies,  $G^E$  and the molar excess enthalpies,  $H^E$ . The sources of available experimental data

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and some characteristic values are collected in Tables 1, 2, and 3. The direct experimental isothermal  $P$ - $x$  or  $P$ - $x$ - $y$  data have been reduced to obtain the molar excess Gibbs energies,  $G^E$ , using the two or three parameters Redlich–Kister equation. Vapour phase imperfection was accounted for in terms of the second virial coefficient estimated by the Hayden and O’Connell [14] method.

$G^E$  data regarding nitroalkanes are really scarce; a only system containing nitromethane and benzene has been studied by Brown and Smith [15] and by Nigam [16]; these data are quite contradictory. Similar data concerning mixtures in tetrachloromethane refers to the first three terms of the series of linear nitroalkanes.

$H^E$  data are more abundant; at least a determination at 298.15 K is available for each 1-nitroalkane (of general formula:  $\text{CH}_3-(\text{CH}_2)_{t-1}-\text{NO}_2$ ;  $t = 1, 2, 3, \dots, 6$ ) + benzene mixture. Experimental enthalpies at equimolar composition concerning nitromethane + benzene at different temperatures do not show a coherent trend. The data of heat of mixing concerning mixtures of nitro-compounds having 4, 5, 6 carbon atoms and tetrachloromethane were necessary to complete the series. Activity coefficients at infinite dilution were available, at different temperatures, for the first three terms of nitroalkanes with both solvents.

## Experimental

### Materials

Chemicals having the properties listed in Table 4, of the highest purity available in the market, were used as received.

### Instrumentation

Heats of mixing were determined by means of a flow micro-calorimeter (model 2277, LKB-producer AB, Bromma,

Sweden). The apparatus and the experimental procedure are described in detail elsewhere [17]. Fully automatic burettes (ABU80, Radiometer, Copenhagen) were used to pump the liquid into the LKB unit. The molar flow rate  $m_i$  ( $\text{mol s}^{-1}$ ), of component  $i$  flowing into the mixing cell is given by:

$$m_i = \frac{\Phi_i \rho_i}{M_i} \quad (1)$$

where  $\Phi_i$  is the volumetric flow rate,  $\rho_i$  the density and  $M_i$  the molar mass. The necessary densities were determined with a vibrating tube densimeter (Anton Paar, model DMA 58) with a reproducibility of  $1 \times 10^{-5} \text{ g cm}^{-3}$ .

The molar excess enthalpies have been evaluated from the formula

$$H^E = \frac{I^2 R (E/E_c)}{m_i} \quad (2)$$

where  $I$  and  $R$  are the electrical current and resistance in the electrical calibration experiment,  $E$  and  $E_c$  are the voltage readings for measurement and electrical calibration, respectively, and  $m$  is the molar flow rate of the mixture. All enthalpy measurements were carried out at 298.15 K. The accuracy of the LKB bath temperature is 0.1 K. The reliability of the apparatus and procedure adopted were checked by performing  $H^E$  measurements on the test system benzene + tetrachloromethane. Our results concerning this system differed by <2% from reliable literature data [18] over the entire composition range.

## Experimental results and discussion

The experimental  $H^E$  data of the binary mixtures containing nitroalkanes of general formula  $\text{CH}_3-(\text{CH}_2)_{n-1}-\text{NO}_2$  (for  $n = 4, 5, 6$ ) with benzene or tetrachloromethane are collected in Table 5. The  $H^E$  values were fitted to the smoothing Redlich–Kister equation:

**Table 1** Molar excess Gibbs energies,  $G^E$  ( $T, x_1 = 0.5$ ), of nitroalkane (1) + benzene or + tetrachloromethane (2) mixtures at various temperatures,  $T$ , and equimolar composition: comparison of direct experimental results (exp) with values calculated (calc) using the coefficients  $C_{uv,l}^{\text{dis}}$  and  $C_{uv,l}^{\text{quac}}$  from Tables 9 and 10

Component (1)	Component (2)	$T/\text{K}$	$G^E$ ( $T, x_1 = 0.5$ )/ $\text{J mol}^{-1}$		Source of experimental data
			Calc	Exp	
Nitromethane	Benzene	318.15	761	759 <sup>a</sup>	[15]
				540 <sup>a</sup>	[16]
Nitromethane	Tetrachloromethane	318.15	1338	1335	[15]
Nitroethane	Tetrachloromethane	298.15	822	820 <sup>a</sup>	[28]
Nitropropane	Tetrachloromethane	298.15	594	591 <sup>a</sup>	[28]

<sup>a</sup> Calculation (this work) by reduction of the original  $P$ - $x$  or  $P$ - $x$ - $y$  data with the 2- or 3-parameters Redlich–Kister equation, vapour phase non-ideality corrected in terms of the second virial coefficient

**Table 2** Molar excess enthalpies,  $H^E(T, x_1 = 0.5)$ , of nitroalkane (1) + benzene or + tetrachloromethane (2) mixtures at various temperatures,  $T$ , and equimolar composition: comparison of direct experimental results (exp) with values calculated (calc) using the coefficients  $C_{uv,l}^{dis}$  and  $C_{uv,l}^{quac}$  from Tables 9 and 10

Component (1)	Component (2)	$T/K$	$H^E(T, x_1 = 0.5)/J \text{ mol}^{-1}$		Source of experimental data	
			Calc	Exp		
Nitromethane	Benzene	298.15	824	791	[29]	
				822	[30]	
		303.15	802	1154	[31]	
			758	914	[31]	
			318.15	737	801	[30]
				824	814	[16]
Nitroethane	Benzene	298.15	267	268	[30]	
				277	[29]	
1-Nitropropane	Benzene	298.15	61	64	[33]	
				63	[29]	
1-Nitrobutane	Benzene	318.15	2	57	[33]	
				298.15	-27	-27
1-Nitropentane	Benzene	298.15	-97	-27	This work	
				-110	[29]	
1-Nitrohexane	Benzene	298.15	-122	-99	This work	
				-122	[29]	
Nitromethane	Tetrachloromethane	298.15	1439	-122	This work	
				1333	[30]	
				1421	[30]	
Nitroethane	Tetrachloromethane	318.15	1426	1426	[32]	
				749	[30]	
				744	[30]	
1-Nitropropane	Tetrachloromethane	298.15	431	429	[33]	
				442	[33]	
1-Nitrobutane	Tetrachloromethane	298.15	277	280	This work	
1-Nitropentane	Tetrachloromethane	298.15	183	185	This work	
1-Nitrohexane	Tetrachloromethane	298.15	137	136	This work	

$$H^E = x_1 x_2 \sum_{i=0}^{n-1} a_i (x_1 - x_2)^i \quad (3)$$

with four parameters, where  $x_1$  is the mole fraction of the nitroalkane and  $n$  is the number of coefficients. The values of the coefficients  $a_i$  and the standard deviation of the fit,  $\sigma(H^E)$ :

$$\sigma(H^E) = \sqrt{\frac{\sum (H_{i,calc}^E - H_{i,exp}^E)^2}{N - n}} \quad (4)$$

obtained by a least squares treatment, are given in Table 6.  $N$  is the number of experimental points.

The obtained experimental results show that all systems containing benzene are, generally, weakly exothermic;  $H^E$ s are higher than  $-122 \text{ J mol}^{-1}$ . 1-Nitrobutane + benzene mixture presents a peculiar shape of the excess enthalpy

curve. A similar behaviour is quite rare but similar examples can be found in literature: see for example the case of 2-butanone + benzene [19, 20]. Nitroalkanes mixed with tetrachloromethane present an endothermic effect with maximum values of mixing heat higher than in the previous case;  $H^E$ s are lower than  $376 \text{ J mol}^{-1}$ . The relative curves are very asymmetric and the  $x_1$  corresponding to the apex are approximately 0.25, 0.22 and 0.20 for 1-nitrobutane, 1-nitropentane and 1-nitrohexane, respectively.

## Theory

Each class of mixtures under examination: nitroalkane + benzene and nitroalkane + tetrachloromethane are regarded as possessing three types of contact surfaces among the following: type a, aliphatic ( $\text{CH}_3$  and  $\text{CH}_2$

**Table 3** Logarithm of activity coefficients at infinite dilution,  $\ln \gamma_i^\infty$ , of constituents the nitroalkane (1) + benzene or + tetrachloromethane (2) mixtures at various temperatures,  $T$ : comparison of direct experimental results (exp) with values calculated (calc) using the coefficients  $C_{uv,l}^{\text{dis}}$  and  $C_{uv,l}^{\text{quac}}$  from Tables 9 and 10

Component (1)	Component (2)	$T/K$	$\ln \gamma_i^\infty$		Source of experimental data	$\ln \gamma_2^\infty$		Source of experimental data
			Calc	Exp		Calc	Exp	
Nitromethane	Benzene	293.15	1.17	1.27	[34]	1.39	1.35	[35]
		318.15	1.27	1.25	[35]	–	–	[36]
		358.85	–	–		1.13	1.12	[36]
		371.45	–	–		1.10	0.97	[36]
Nitroethane	Benzene	293.15	0.48	0.81	[34]	0.45	0.60	[36]
1-Nitropropane	Benzene	298.15	0.02	0.67	[34]	0.01	0.03	[37]
Nitromethane	Tetrachloromethane	293.15	2.56	2.72	[35]	2.36	2.18	[35]
							2.26	[34]
		314.85	2.32	2.46	[36]	–	–	
		328.25	2.19	2.37	[36]	–	–	
		340.50	2.09	2.21	[36]	–	–	
		349.05	2.02	2.13	[36]	–	–	
Nitroethane	Tetrachloromethane	293.15		–		1.20	1.21	[34]
				–		1.20	1.37	[35]
1-Nitropropane	Tetrachloromethane	293.15		–		0.77	0.81	[34]

**Table 4** Supplier, molar masses, purities and densities at 298.15 K of chemicals used in the experiments

Compound	Supplier	$M/\text{g mol}^{-1}$	Purity/%	$\rho_{\text{exp}}/\text{kg m}^{-3}$	$\rho_{\text{lit}}/\text{kg m}^{-3}$	Source of experimental data
1-Nitrobutane	Aldrich	103.12	98	968.43	970	[38]
1-Nitropentane	Aldrich	117.15	97	949.30	952.5 <sup>a</sup>	[38]
1-Nitrohexane	Aldrich	131.17	98	935.64	939.6 <sup>a</sup>	[38]
Benzene	Riedel de Haën	78.11	99.7	874.51	873.60	[12]
Tetrachloromethane	Riedel de Haën	153.82	99.8	1584.24	1584.36	[12]

<sup>a</sup> Measured at 293.15 K

groups in linear nitroalkanes), type n, nitro group ( $\text{NO}_2$  in nitroalkanes), type b, benzene ( $\text{C}_6\text{H}_6$ ) and type d, tetrachloromethane ( $\text{CCl}_4$ ). Benzene and tetrachloromethane are considered homogeneous molecules. The equations used to calculate  $G^E$  and  $H^E$  in terms of DISQUAC are the same as in other applications [1] and need not be repeated here.

The dispersive and the quasichemical interchange coefficients, concerning a contact among two different type of surfaces,  $C_{uv,l}^{\text{dis}}$  and  $C_{uv,l}^{\text{quac}}$  where  $u, v = a, b, n, d$  and  $l = 1$  (Gibbs energy) or  $l = 2$  (enthalpy) express the strength of interaction among different groups. Heat capacity coefficients,  $l = 3$ , have not been considered.

#### Assessment of geometrical parameters

The relative geometrical parameters as volumes,  $r_i$ , surfaces,  $q_i$ , and, molecular surface fractions  $\alpha_{vi}$ , of all the

molecular species have been calculated on the basis of the relative group parameters, the volumes,  $r_G$ , and surfaces,  $q_G$ , taking arbitrarily the volume,  $V_{\text{CH}_4}$ , and surface,  $A_{\text{CH}_4}$ , of methane as unity. Thus  $r_G = V_G/V_{\text{CH}_4}$  and  $q_G = A_G/A_{\text{CH}_4}$ . In general, the  $V_G$  and  $A_G$  values calculated by Bondi [21] have been adopted. The relative group parameters used in this work are reported in Table 7. Table 8 lists the geometrical parameters of all compounds referred to in this paper.

#### Estimation of interaction parameters

The groups investigated in the present work are non polar (type a), polarizable (type b and d) or polar (type n).

To improve the prediction, in the application of the model, we make assumption that the parameters may vary with the molecular structure, in particular for the first members of homologous series. The variation should be

**Table 5** Experimental values of the molar excess enthalpies,  $H^E$ , of binary mixtures of nitroalkanes (1) + benzene or + tetrachloromethane (2) at 298.15 K

$x_1$	$H^E/J \text{ mol}^{-1}$	$x_1$	$H^E/J \text{ mol}^{-1}$	$x_1$	$H^E/J \text{ mol}^{-1}$
Nitrobutane + benzene					
0.0530	4.7	0.3865	-28.8	0.7706	-5.1
0.0775	3.3	0.4565	-28.5	0.8344	-0.9
0.0950	0.6	0.5283	-22.8	0.8704	0.8
0.1228	-4.6	0.5575	-20.8	0.8936	1.4
0.1735	-12.1	0.6268	-16.6	0.9097	1.8
0.2187	-20.7	0.6913	-10.7		
0.2957	-26.3	0.7159	-9.1		
Nitropentane + benzene					
0.1077	-27.7	0.4199	-99.6	0.8128	-45.5
0.1944	-61.5	0.5206	-96.6	0.8786	-30.1
0.2658	-80.5	0.5915	-90.6		
0.3519	-94.3	0.6847	-72.9		
Nitrohexane + benzene					
0.0960	-27.3	0.3892	-119.4	0.6565	-99.9
0.1752	-64.2	0.4593	-122.0	0.7927	-63.8
0.2416	-85.0	0.4887	-118.3	0.8644	-45.0
0.2981	-107.0	0.5603	-117.4		
Nitrobutane + tetrachloromethane					
0.1856	363.7	0.4769	293.3	0.7848	102.3
0.2331	376.1	0.5487	252.6	0.8455	69.9
0.3131	367.4	0.6458	191.1		
0.3781	347.8	0.7323	136.6		
Nitropentane + tetrachloromethane					
0.1161	250.3	0.4409	221.3	0.7029	80.1
0.1647	291.7	0.5125	180.3	0.7593	56.8
0.2828	290.0	0.5419	165.7	0.8255	36.7
0.3716	247.6	0.6119	126.8		
Nitrohexane + tetrachloromethane					
0.1035	226.9	0.3159	227.0	0.5807	96.4
0.1476	244.1	0.4092	178.4	0.6751	64.0
0.1876	251.3	0.4801	150.1	0.7869	28.7
0.2062	249.0	0.5095	138.6	0.8471	16.3

**Table 6** Values of the coefficients,  $a_i$ , standard deviations,  $\sigma$  ( $H^E$ ), of molar excess enthalpies,  $H^E$  at 298.15 K, for nitroalkanes (1) + benzene or + tetrachloromethane (2) mixtures

Mixtures	$a_0/J \text{ mol}^{-1}$	$a_1/J \text{ mol}^{-1}$	$a_2/J \text{ mol}^{-1}$	$a_3/J \text{ mol}^{-1}$	$\sigma (H^E)/J \text{ mol}^{-1}$
1-Nitrobutane + benzene	-107.74	133.56	157.86	-192.3	2.0
1-Nitropentane + benzene	-396.91	131.2	156.46	-183.97	1.8
1-Nitrohexane + benzene	-86.09	134.42	182.76	-245.97	2.8
1-Nitrobutane + tetrachloromethane	1119.8	-1176.5	910.9	-685.69	2.4
1-Nitropentane + tetrachloromethane	738.97	-1070.3	918.1	-756.02	4.4
1-Nitrohexane + tetrachloromethane	543.12	-881.38	953.58	-902.6	7.7

**Table 7** Relative group increments for molecular volumes,  $r_G = V_G/V_{\text{CH}_4}$  and areas,  $q_G = A_G/A_{\text{CH}_4}$  ( $V_{\text{CH}_4} = 17.12 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ ,  $A_{\text{CH}_4} = 2.90 \times 10^5 \text{ m}^2 \text{ mol}^{-1}$ )

Group	$r_G$	$q_G$
-CH <sub>3</sub>	0.79848	0.73103
-CH <sub>2</sub> -	0.59755	0.46552
-NO <sub>2</sub>	0.98132	0.87930

regular and similar classes should follow the same rules. The final selection of parameters is achieved by plotting the, usually few, adjusted values on smooth curves and estimating the other values by interpolation or extrapolation.

In this section we formulate the rules and list the selected values of the coefficients.

Every class of mixtures is characterized by three types of contacts; (a,b), (a,n) and (b,n) for mixtures with benzene and (a,n) (a,d) and (d,n) for mixtures with tetrachloromethane. In this work the interchange parameters for the contacts (b,n) and (d,n) have been determined while the parameters for the remaining contacts were taken from the literature.

The rules we found as follows:

#### 1. Nitroalkane + benzene

(1a) (a,b)-contact. DIS. The  $C_{ab,1}^{\text{dis}}$  dispersive coefficients were assumed constant for every system. The values taken from the literature [22] are:  $C_{ab,1}^{\text{dis}} = 0.26$  and  $C_{ab,2}^{\text{dis}} = 0.56$ .

(1b) (a,n)-contact. DISQUAC. The interchange coefficients, dispersive and quasi-chemical, calculated independently from properties of nitroalkanes + *n*-alkane mixtures can be used [13]. The dispersive coefficients are constant for all linear 1-nitroalkanes,  $C_{an,1}^{\text{dis}} = 1.00$  and  $C_{an,2}^{\text{dis}} = 1.70$ . The quasi-chemical coefficients decrease as the length of the molecule increases:  $C_{an,1}^{\text{quac}}$  values are in the range  $4.80 \div 4.00$  and  $C_{an,2}^{\text{quac}}$  values are in the range  $7.40 \div 5.40$ .

**Table 8** Relative volumes,  $r_i$ , relative total surfaces,  $q_i$ , and molecular surface fractions,  $\alpha_{vi}$ , ( $v = a, b, n, d$ ) calculated from the group increments  $r_G$  and  $q_G$  given in Table 7; a (CH<sub>3</sub>, CH<sub>2</sub>); n (NO<sub>2</sub>); b (C<sub>6</sub>H<sub>6</sub>); d (CCl<sub>4</sub>)

Compound	$r_i$	$q_i$	$\alpha_{ai}$	$\alpha_{ni}$	$\alpha_{bi}$	$\alpha_{di}$
Nitromethane	1.7798	1.6103	0.4540	0.5460	0.0000	0.0000
Nitroethane	2.3773	2.0759	0.5764	0.4236	0.0000	0.0000
1-Nitropropane	2.9749	2.5414	0.6540	0.3460	0.0000	0.0000
1-Nitrobutane	3.5724	3.0069	0.7076	0.2924	0.0000	0.0000
1-Nitropentane	4.1700	3.4724	0.7468	0.2532	0.0000	0.0000
1-Nitrohexane	4.7676	3.9379	0.7767	0.2933	0.0000	0.0000
Benzene	2.8248	2.0724	0.0000	0.0000	1.0000	0.0000
Tetrachloromethane	3.0543	2.5104	0.0000	0.0000	0.0000	1.0000

**Table 9** Dispersive and quasicheical interchange energy coefficients for contact (b,n) in linear nitroalkanes (1) + benzene (2) mixtures

Component (1)	$C_{bn,1}^{dis}$	$C_{bn,2}^{dis}$	$C_{bn,1}^{quac}$	$C_{bn,2}^{quac}$
Nitromethane	2.21	2.43	1.0	0.9
Nitroethane	1.59 <sup>a</sup>	1.75	1.0 <sup>a</sup>	0.9
1-Nitropropane	1.20 <sup>a</sup>	1.29	1.0 <sup>a</sup>	0.9
1-Nitrobutane	1.16 <sup>a</sup>	1.12	1.0 <sup>a</sup>	0.9
1-Nitropentane	1.13 <sup>a</sup>	0.91	1.0 <sup>a</sup>	0.9
1-Nitrohexane	1.00 <sup>a</sup>	0.76	1.0 <sup>a</sup>	0.9

<sup>a</sup> Gussed value**Table 10** Dispersive and quasicheical interchange energy coefficients for contact (d,n) in linear nitroalkanes (1) + tetrachloromethane (2) mixtures

Component (1)	$C_{dn,1}^{dis}$	$C_{dn,2}^{dis}$	$C_{dn,1}^{quac}$	$C_{dn,2}^{quac}$
Nitromethane	0.62	1.68	4.3	4.4
Nitroethane	0.12	0.97	4.3	4.5
1-Nitropropane	-0.03	0.35	4.3	4.8
1-Nitrobutane	-0.03 <sup>a</sup>	-0.16	4.3 <sup>a</sup>	5.4
1-Nitropentane	-0.03 <sup>a</sup>	-0.71	4.3 <sup>a</sup>	6.1
1-Nitrohexane	-0.03 <sup>a</sup>	-1.41	4.3 <sup>a</sup>	7.1

<sup>a</sup> Gussed value

(1c) (b,n)-contact. DISQUAC. All coefficients values concerning the (b,n)-contact are presented in Table 9. The dispersive coefficients,  $C_{bn,1}^{dis}$ , show a decreasing trend as the length of the alkyl chain of nitroalkane increases. The Gibbs energy parameters,  $C_{bn,1}^{dis}$ , values are in the range 2.21 ÷ 1.00 but because of the lack of experimental data most of them are estimated. The values of the enthalpic parameters,  $C_{bn,1}^{dis}$ , are comprise between 2.53 for nitromethane and 0.76 for 1-nitrohexane.

The quasicheical coefficients,  $C_{bn,1}^{quac} = 1.0$ ,  $C_{bn,2}^{quac} = 0.9$ , are constant and independent of the chain length of the  $n$ -alkyl groups adjacent to the nitro group.

## 2. Nitroalkane + tetrachloromethane

(2a) (a,d)-contact. DIS. The  $C_{ad,1}^{dis}$ , dispersive coefficients were assumed constant for every system. The values taken from the literature [23] are:  $C_{ab,1}^{dis} = 0.093$  and  $C_{ab,2}^{dis} = 0.18$ .

(2b) (a,n)-contact. See above, rule (1b).

(2c) (d,n)-contact. DISQUAC. All coefficients values concerning the (d,n)-contact are presented in Table 10. The dispersive coefficients,  $C_{dn,1}^{dis}$ ,

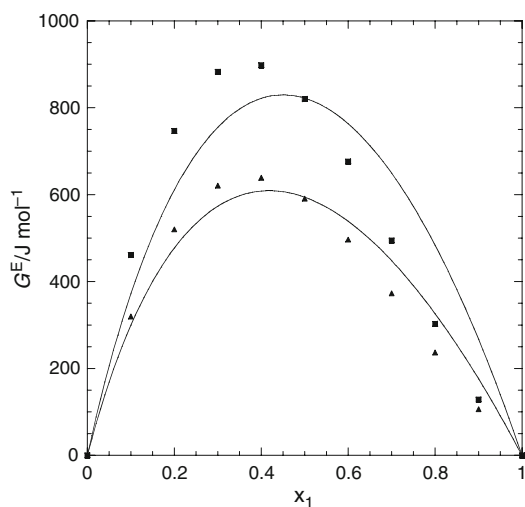
shows a decreasing trend as the length of the alkyl chain of nitroalkane increases. The Gibbs energy parameters,  $C_{dn,1}^{dis}$ , values vary from 0.62 for nitromethane to -0.03 for 1-nitro-propane, -butane, -pentane, -hexane. In Table 10 also are reported some estimated results. The values of the enthalpic parameters,  $C_{dn,1}^{dis}$ , are comprise between 1.68 for nitromethane and -1.41 for 1-nitrohexane.

The first quasicheical coefficients,  $C_{dn,1}^{quac} = 4.3$ , is independent of the chain length of the  $n$ -alkyl groups adjacent to the nitro group. The second quasicheical coefficients,  $C_{dn,2}^{quac}$ , vary in the range: 4.4 ÷ 7.1.

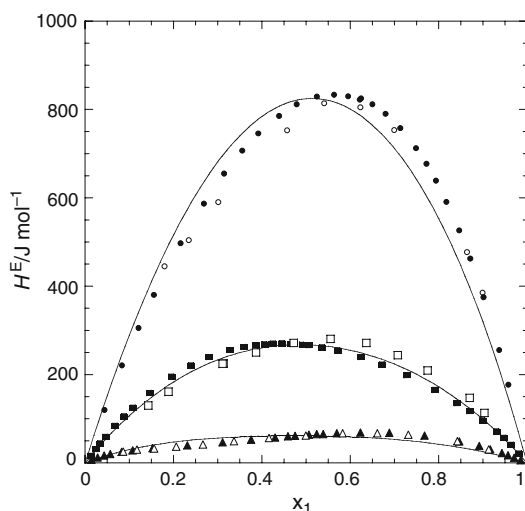
## Comparison with experiment and discussion

In this session we discuss the physical meaning of the observed rules and compare the calculated data with experiments.

Sometimes polar/polar or polar/polarizable groups contacts are correctly described by an entirely dispersive approach [24, 25]. This is possible when intermolecular force exerted by the two different groups are similar. In the



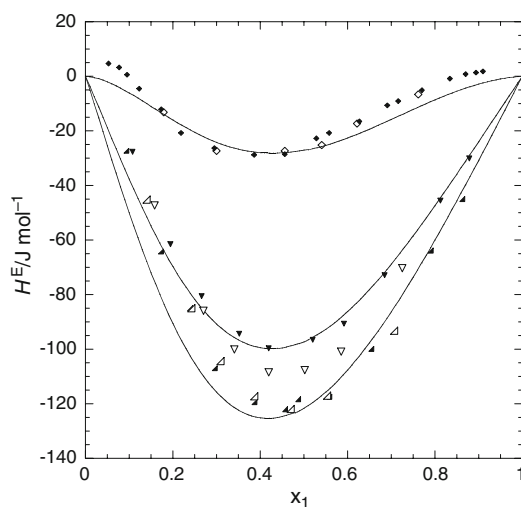
**Fig. 1** Comparison of theory with experiments for the molar excess Gibbs energies,  $G^E$ , at 298.15 K, for nitroalkanes (1) + tetrachloromethane (2) mixtures versus  $x_1$ , the mole fraction of component (1): *full lines*, DISQUAC predictions; *points*, experimental results from Ref. [28]; ■, 1-nitroethane; ▲, 1-nitropropane



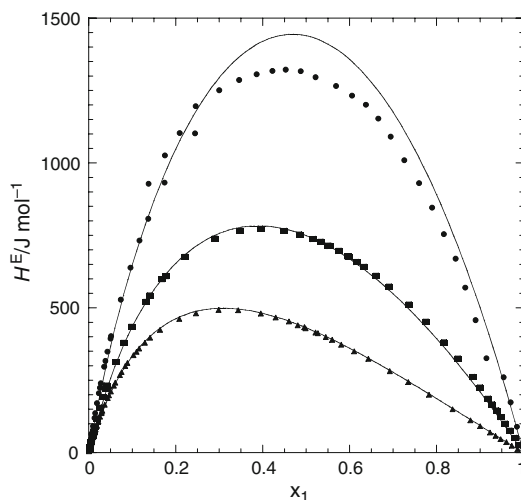
**Fig. 2** Comparison of theory with experiments for the molar excess enthalpies,  $H^E$ , at 298.15 K, for nitroalkanes (1) + benzene (2) mixtures versus  $x_1$ , the mole fraction of component (1): *full lines*, DISQUAC predictions; *points*, experimental results: ●, nitromethane [30]; ○, nitromethane [29]; ■, 1-nitroethane [30]; □, 1-nitroethane [29]; ▲, 1-nitropropane [33]; △, 1-nitropropane [29]

case of the two classes of mixtures under investigation R-NO<sub>2</sub> + B and R-NO<sub>2</sub> + T, it has been necessary to consider also a quasicheical contribution. A such approach has been adopted, for example, for alkanenitrile + chloroalkanes mixtures [26].

The dispersive interchange parameters relative to the n group/benzene or tetrachloromethane exhibits exactly the same trend: they decrease as the length of alkyl group of the nitro-compound increase. In the case of mixtures in T



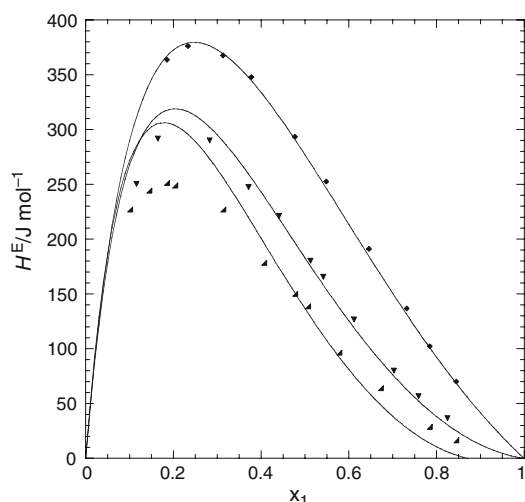
**Fig. 3** Comparison of theory with experiments for the molar excess enthalpies,  $H^E$ , at 298.15 K, for nitroalkanes (1) + benzene (2) mixtures versus  $x_1$ , the mole fraction of component (1): *full lines*, DISQUAC predictions; *points*, experimental results: ◆, 1-nitrobutane [this work]; ◇, 1-nitrobutane [29]; ▼, 1-nitropentane [this work]; ▽, 1-nitropentane [29]; ▲, 1-nitrohexane [this work]; ◄, 1-nitrohexane [29]



**Fig. 4** Comparison of theory with experiments for the molar excess enthalpies,  $H^E$ , at 298.15 K, for nitroalkanes (1) + tetrachloromethane (2) mixtures versus  $x_1$ , the mole fraction of component (1): *full lines*, DISQUAC predictions; *points*, experimental results: ●, nitromethane [30]; ■, 1-nitroethane [30]; ▲, 1-nitropropane [33]

they became negative for the heavier nitro-compounds here considered. Negative parameters have been obtained also for the contact alkene group/T [27]. The quasicheical parameters,  $C_{sn,1}^{quac}$ , where  $s = b, d$ , are constant with the exception of  $C_{dn,2}^{quac}$  that increase as the Carbon atoms number in the polar compound increases.

The influence of the inductive and steric effect of an alkyl group adjacent to a polar X group ( $X = \text{NO}_2$ ) on the dispersive and quasi-chemical interchange parameters



**Fig. 5** Comparison of theory with experiments for the molar excess enthalpies,  $H^E$ , at 298.15 K, for nitroalkanes (1) + tetrachloromethane (2) mixtures versus  $x_1$ , the mole fraction of component (1): *full lines*, DISQUAC predictions; *points*, experimental results from this work:  $\blacklozenge$ , 1-nitrobutane;  $\blacktriangledown$ , 1-nitropentane;  $\blacktriangle$ , 1-nitrohexane

$C_{sx,l}^{quac}$  can be more easily explained if we consider that the interchange energies,  $\Delta\varepsilon_{sx}$ , are related to the interaction energies,  $\varepsilon_{sx}$ ,

$$\Delta\varepsilon_{sx} = \frac{(|\varepsilon_{ss}| + |\varepsilon_{xx}|)}{2} - |\varepsilon_{sx}| \quad (5)$$

the  $\varepsilon$  values being negative.

In polar–polar/polarizable systems the inductive effect exerted by an alkyl group adjacent to the polar X group increases the dispersive interaction energies  $\varepsilon_{sx}$  and consequently decreases  $\Delta\varepsilon_{sx}$  and  $C_{sx,l}^{dis}$ , i.e. the dispersive coefficients of the nitro group/polarisable contact.

The steric effect acts mainly on the quasi-chemical parameters. In polar–polar/polarizable systems it decreases the electrostatic energies  $\varepsilon_{sx}$  and consequently increases  $\Delta\varepsilon_{sx}$  and  $C_{sx,l}^{quac}$ , the quasicheical parameters of the nitro group/polarisable contact.

The systems here considered show moderate deviations from ideality. Indeed,  $G^E$  at equimolar composition for the mixtures under examination are approximately in the range  $+1375 \div +540 \text{ J mol}^{-1}$ , meanwhile  $H^E$  vary between  $+1426$  and  $-122 \text{ J mol}^{-1}$ . Heat of mixing at 298.15 K and equimolar composition, generally positive, decrease as the length of the alkyl chain of the nitro-compound increase (and became negative in the case of mixtures in benzene of nitrobutane, nitropentane and nitrohexane).

The few data concerning excess Gibbs energy curves versus  $x_1$  obtained from VLE measurements are reproduced in an approximate way. See for example Fig. 1 where are reported data that refers to nitroethane and 1-nitropropane + tetrachloromethane.

$H^E$ s values are generally reproduced quite well by the DISQUAC model. In Figs. 2 and 3 are considered mixtures containing benzene and in Figs. 4 and 5 mixtures with tetrachloromethane.

The trend of the skew  $H^E$  curve of 1-nitrohexane + T was particularly difficult to reproduce. The overall agreement represented in Fig. 5 is however satisfying.

The temperature dependence is roughly reproduced by the model even if not at the correct extend. This result was expected because the  $H^E$  values have been calculated with zero heat capacity of dispersive and quasi-chemical interchange coefficients.

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