Calorimetric Study of Nitrile Group−Solvent Interactions and Comparison with Dispersive Quasi-Chemical (DISQUAC) Predictions[†]

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A flow microcalorimeter, model 2277-LKB, has been used to determine excess enthalpies, H^E, at 298.15 K, for liquid mixtures containing ethanenitrile, propanenitrile, butanentrile, or pentanenitrile + benzene or tetrachloromethane. These experimental results together with the literature data on thermodynamic properties of alkanenitrile + benzene or tetrachloromethane mixtures have been interpreted in terms of the dispersive quasi-chemical (DISQUAC) group contribution model. Two sets of structure-dependent interaction parameters, for the nitrile group/aromatic and for the nitrile group/tetrachloromethane contacts, have been obtained. The model provides a fairly consistent description of the excess Gibbs energy, G^E, excess enthalpy, H^E, and of activity coefficients at infinite dilution, γ_i^∞, of the considered mixtures.

Introduction

Group contribution models have been introduced to predict thermodynamic properties of binary mixtures. Accurate calculations, at present, are not possible without the use of at least a limited number of experimental data concerning at least a few mixtures. Because of the characteristic of the liquid model adopted, these studies have been chiefly limited to classes of organic compounds. The studies developed around such models have greatly contributed to extend and correlate the mixing properties databanks.

Our research group, since 1982, has been involved in the frame of the TOM Project[1] in the systematic study to organic mixtures of the dispersive quasi-chemical (DISQUAC) model,[2,3] the group contribution model developed by Henry Kehiaian since 1978, on the basis of the Guggenheim's rigid lattice theory.[4]

DISQUAC calculates the excess thermodynamic properties as a sum of two contributions: one, DIS, due to dispersive forces, always present, whatever the kind of molecules, and another, QUAC, depending on specific chemical interactions.

Following a coherent strategy, in the application of the model, we first examined mixtures of organic compounds of different polarity with linear and cyclic alkanes. Then mixtures containing the same classes previously studied with a different second component having a moderate polarizability such as benzene and tetrachloromethane or other chemicals belonging to a given different class of compounds.

Alkanenitriles are organic compounds that have found applications in different fields. Ethanenitrile is one of the most used solvents in chemical and biological laboratories and in industrial processes. Nitriles are characterized by a high polarity, practically independent from the length of the alkyl chain; dipolar moments of ethanenitrile and propanenitrile in benzene at 293 K are (3.53 and 3.50) D, respectively.[5]

In previous papers the authors reported the results of the application of the DISQUAC model on alkanenitrile-containing mixtures with the following compounds: linear alkanes and cyclohexane,[6] 1-chloroalkanes,[7] and tetrahydrofuran and cyclohexane in a three-component system.[8]

In this work we report the results concerning the experimental determination of the H^E at 298.15 K for mixtures containing an alkanenitrile of general formula: $CH_3(CH_2)_{u-2}CN$ ($u = 2, 3, 4, 5$) + benzene or + tetrachloromethane. Most of them were necessary to complete the set of thermodynamic data used in the DISQUAC analysis on alkanenitrile + benzene and on alkanenitrile + tetrachloromethane also presented in this work.

Data used in the model application are concerned with vapor−liquid equilibria and correlated excess Gibbs energies, G^E, excess enthalpies, H^E, and activity coefficients at infinite dilution, γ_i^∞.

The sources of available experimental data and some characteristic values are collected in Tables 1 to 3.[9−29] 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-parameter Redlich−Kister equation. Vapor phase imperfection was accounted for in terms of the second virial coefficient estimated by the Hayden and O'Connell[30] method.

G^E data regarding alkanenitriles are scarce; concerning benzene-containing mixtures, we found three sources: Srivastava and Smith,[9] Brown and Smith,[10] and Artal et al.[11] The only reference on G^E for the ethanenitrile + tetrachloromethane mixtures was found in the literature.[12] H^E data, mostly concerning ethanenitrile + benzene at different temperatures,[13−22] are more abundant. H^E data were available for butanenitrile + benzene[23] and for ethanenitrile + tetrachloromethane.[14,19,22] For the last system cited, a value of H^E at 318.15 K dated 1956 is also given. Activity coefficients at infinite dilution were available, at different temperatures, concerning the first four terms of the series of linear alkanenitriles with benzene[25−28] and for ethane- and propanenitrile + tetrachloromethane.[24−26,29]

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Table 1. Molar Excess Gibbs Energies, G^E (T, $x_1 = 0.5$), of Alkanenitrile (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 $C^{\text{dis}}_{\text{uv,l}}$ and $C^{\text{quac}}_{\text{uv,l}}$ from Table 9

			G^E (T, $x_1 = 0.5$)/J·mol^{-1}		
component (1)	component (2)	T/K	calc	exp[a]	source of exptl data
ethanenitrile	benzene	298.15	647	647	9
		318.15	663	673	10
		348.15	695	645	9
		398.15	764	661	9
propanenitrile	benzene	318.15	370	369	11
butanenitrile	benzene	318.15	220	222	11
ethanenitrile	tetrachloromethane	318.15	1187	1190	12

[a] Calculation (this work) by reduction of the original P,x or P,x,y data with the two- or three-parameter Redlich−Kister equation, with the vapor phase nonideality corrected in terms of the second virial coefficient.

Table 2. Molar Excess Enthalpies, H^E (T, $x_1 = 0.5$), of Alkanenitrile (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 $C^{\text{dis}}_{\text{uv,l}}$ and $C^{\text{quac}}_{\text{uv,l}}$ from Table 9

			H^E (T, $x_1 = 0.5$)/J·mol^{-1}		
component (1)	component (2)	T/K	calc	exp	source of exptl data
ethanenitrile	benzene	298.15	438	438	this work
				448	13
				444	14
				449	15
				465	16
				449	17
		303.15	420	442	18
		314.35	383	476	15
		318.15	370	476	19
				482	20
				480	21
				490	22
propanenitrile		298.15	69	68	this work
butanenitrile		298.15	−64	−66	this work
				−57	23
pentanenitrile		298.15	−109	−112	this work
ethanenitrile	tetrachloromethane	298.15	757	755	this work
				773	14
		318.15	749	897	19
				913	22
propanenitrile		298.15	309	309	this work
butanenitrile		298.15	100	98	this work
pentanenitrile		298.15	−28	−31	this work

Table 3. Logarithm of Activity Coefficients at Infinite Dilution, ln γ_i^∞, of Alkanenitrile (1) + Benzene or Tetrachloromethane (2) Mixtures at Various Temperatures, T: Comparison of Direct Experimental Results (exp) with Values Calculated (calc) Using the Coefficients $C^{\text{dis}}_{\text{uv,l}}$ and $C^{\text{quac}}_{\text{uv,l}}$ from Table 9

			ln γ_1^∞			ln γ_2^∞		
component (1)	component (2)	T/K	calc	exp	source of exptl data	calc	exp	source of exptl data
ethanenitrile	benzene	293.15	1.06	1.20	24			
		293.15		1.24	25			
		298.15				1.08	1.16	25
		318.15	1.03	1.12	26	1.03	1.08	26
		373.15	0.97	1.27	27			
propanenitrile	benzene	293.15	0.65	0.82		0.52	0.61	25
		298.15	0.65	0.47	28			
butanentrile	benzene	298.15	0.42	0.29	28			
pentanenitrile	benzene	298.15				0.18	0.07	27
ethanenitrile	tetrachloromethane	293.15	2.56	2.60	25	2.04	1.90	25
							1.89	24
		298.15				2.02	1.85	29
		314.85	2.38	2.37	26			
		316.45	2.37	2.31	26			
		329.95	2.28	2.21	26			
		340.15	2.21	2.16	26			
		345.95	2.18	2.09	26			
		352.55				1.88	1.59	26
propanenitrile	tetrachloromethane	293.15				1.34	1.14	25
							1.06	24

Table 4. Supplier, Molar Masses, Purities Expressed as Mole Fraction, and Densities at 298.15 K of Chemicals Used in the Experiments

compound	supplier	$\frac{M}{\mathrm{g \cdot mol^{-1}}}$	purity	$\frac{\rho_{\mathrm{exp}}}{\mathrm{kg \cdot m^{-3}}}$	$\frac{\rho_{\mathrm{lit}}}{\mathrm{kg \cdot m^{-3}}}$	source of exptl data
ethanenitrile	Aldrich	41.052	0.999	776.62	776.49	5
propanenitrile	Aldrich	55.079	0.99	777.69	776.82	5
butanenitrile	Aldrich	69.105	0.99	786.27	786.5	5
pentanenitrile	Aldrich	83.132	0.995	794.79	795.0	5
benzene	Riedel de Haën	78.113	0.997	875.47	873.60	5
tetrachloromethane	Riedel de Haën	153.823	0.998	1584.30	1584.36	5

Table 5. Experimental Values of the Molar Excess Enthalpies, H^{E}, of Binary Mixtures of Alkanenitriles (1) + Benzene or Tetrachloromethane (2) at 298.15 K

x_1	$\frac{H^{\mathrm{E}}}{\mathrm{J \cdot mol^{-1}}}$	x_1	$\frac{H^{\mathrm{E}}}{\mathrm{J \cdot mol^{-1}}}$	x_1	$\frac{H^{\mathrm{E}}}{\mathrm{J \cdot mol^{-1}}}$
		Ethanenitrile + Benzene			
0.2196	239.9	0.5295	441.5	0.8351	318.8
0.2968	319.0	0.6280	452.2	0.8710	269.2
0.3876	376.8	0.7169	423.9	0.9101	202.1
0.4577	428.9	0.7715	398.8		
		Propanenitrile + Benzene			
0.0949	23.7	0.3206	43.4	0.7156	81.9
0.1118	25.3	0.3862	54.3	0.7906	76.2
0.1359	25.5	0.4562	62.4	0.8342	66.8
0.1734	29.9	0.4855	68.2	0.8830	54.0
0.1909	27.9	0.5572	78.4	0.9096	46.2
0.2393	33.8	0.6265	83.1	0.9497	27.7
0.2955	39.3	0.6537	80.0		
		Butanenitrile + Benzene			
0.0922	−15.4	0.3367	−65.8	0.8024	−22.9
0.1126	−24.6	0.4322	−66.6	0.8904	−9.6
0.1447	−33.1	0.5037	−65.9	0.9241	−5.9
0.2024	−45.7	0.5751	−56.2	0.9384	−4.8
0.2528	−57.1	0.6700	−43.4		
0.2757	−61.1	0.7528	−31.2		
		Pentanenitrile + Benzene			
0.0964	−35.5	0.4603	−115.5	0.8366	−45.1
0.1245	−47.8	0.5321	−106.5	0.8722	−35.0
0.1758	−71.1	0.5613	−102.9	0.8951	−28.7
0.2214	−87.6	0.6305	−92.9	0.9110	−23.4
0.2990	−101.7	0.7190	−73.3	0.9275	−19.8
0.3625	−111.7	0.7733	−59.7		
		Ethanenitrile + Tetrachloromethane			
0.1552	538.8	0.4787	777.5	0.7860	485.1
0.1867	587.4	0.5505	754.2	0.8305	428.6
0.2344	649.2	0.6475	653.4	0.8802	320.9
0.3147	715.1	0.7101	598.2	0.9484	156.1
0.3798	739.5	0.7337	584.4		
		Propanenitrile + Tetrachloromethane			
0.1025	275.5	0.4065	355.1	0.7326	184.6
0.1205	316.9	0.4774	325.4	0.7851	138.3
0.1859	355.0	0.5068	311.8	0.8457	101.5
0.2551	370.4	0.6462	235.9	0.9320	51.5
0.3135	372.1	0.6729	222.8		
		Butanenitrile + Tetrachloromethane			
0.0843	191.0	0.3559	172.3	0.6885	4.3
0.0995	204.8	0.4242	142.5	0.7683	−19.6
0.1556	229.3	0.4532	133.3	0.8155	−27.7
0.2165	231.5	0.5250	89.5	0.8690	−26.8
0.2692	220.8	0.5957	53.7	0.9170	−21.5
0.2930	216.6	0.6338	43.6	0.9299	−17.4
		Pentanenitrile + Tetrachloromethane			
0.0718	143.3	0.3170	87.4	0.7358	−107.1
0.0849	152.0	0.3823	49.1	0.7878	−97.3
0.1040	158.5	0.4814	−9.0	0.8478	−82.8
0.1340	161.2	0.5531	−57.2	0.9027	−62.2
0.1884	155.8	0.5820	−63.0	0.9176	−53.6
0.2363	135.0	0.6499	−89.6		

Experimental Section

Materials. Chemicals having the properties listed in Table 4,[5] of the highest purity available in the market, were used as received.

Apparatus and Procedure. Enthalpies of mixing were determined by means of a flow microcalorimeter (model 2277 LKB, producer AB, Bromma, Sweden). The apparatus and the experimental procedure are described in detail elsewhere.[31] Fully automatic burets (ABU80 - Radiometer, Copenhagen, Denmark) were used to pump the liquid into the LKB unit. The molar flow rate, m_{i} ($\mathrm{mol \cdot s^{-1}}$), of component i flowing into the mixing cell is given by:

$$m_{\mathrm{i}} = \frac{\Phi_{\mathrm{i}} \rho_{\mathrm{i}}}{M_{\mathrm{i}}} \qquad (1)$$

where Φ_{i} is the volumetric flow rate, ρ_{i} the density, and M_{i} the molar mass. The necessary densities were determined with a vibrating-tube densitometer (model DMA 58, Anton Paar, Graz, Austria) with a reproducibility of $1 \cdot 10^{-5}\ \mathrm{g \cdot cm^{-3}}$.

The molar excess enthalpies have been evaluated from the formula

$$H^{\mathrm{E}} = \frac{I^2 R(E/E_{\mathrm{c}})}{m_{\mathrm{i}}} \qquad (2)$$

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 uncertainty of the LKB bath temperature is ± 0.1 K. The reliability of the apparatus and procedure adopted were checked periodically by performing H^{E} measurements on the test system benzene + cyclohexane. Our results concerning this system differed by < 2 % from reliable literature data[32] over the entire composition range. The mean value of the combined standard uncertainties ($k = 2$), calculated by using the σ values associated to the best fitting procedure is $13\ \mathrm{J \cdot mol^{-1}}$.

Experimental Results and Discussion

The experimental H^{E} data of the binary mixtures containing, as component (1), an alkanenitrile of the general formula $\mathrm{CH_3(CH_2)_{\mathit{u}-2}CN}$ (for $u = 2, 3, 4, 5$) with benzene or tetrachloromethane, as component (2), are collected in Table 5. The H^{E} values were fitted to the smoothing Redlich−Kister equation:

$$H^{\mathrm{E}} = x_1 x_2 \sum_{\mathrm{i}=0}^{n-1} a_{\mathrm{i}} (x_1 - x_2)^{\mathrm{i}} \qquad (3)$$

with three or four parameters, where x_1 is the mole fraction of the alkanenitrile and n is the number of coefficients. The values of the coefficients a_{i} and the standard deviation of the fit, $\sigma(H^{\mathrm{E}})$:

Table 6. Values of the Coefficients, a_i, and Standard Deviations, $\sigma(H^E)$, of Molar Excess Enthalpies, H^E at 298.15 K, for Alkanenitrile (1) + Benzene or Tetrachloromethane (2) Mixtures

mixture	a_0 / $J \cdot mol^{-1}$	a_1 / $J \cdot mol^{-1}$	a_2 / $J \cdot mol^{-1}$	a_3 / $J \cdot mol^{-1}$	$\sigma(H^E)$ / $J \cdot mol^{-1}$
ethanenitrile + benzene	1751.20	700.10	215.31	0	4.8
propanenitrile + benzene	272.91	275.65	170.05	−145.28	2.2
butanenitrile + benzene	−262.53	166.98	144.39	−134.77	1.8
pentanenitrile + benzene	−446.49	180.84	112.10	−153.29	1.9
ethanenitrile + tetrachloromethane	3019.20	−662.71	993.42	0	15
propanenitrile + tetrachloromethane	1237.00	−918.47	991.02	−756.14	10
butanenitrile + tetrachloromethane	390.50	−1069.90	848.09	−795.48	7.9
pentanenitrile + tetrachloromethane	−125.08	−1048.4	934.94	−766.24	8.6

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

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

Alkanenitriles exhibit a greater affinity toward benzene and tetrachloromethane than toward n-alkanes. Indeed, the nitriles considered here, when mixed with *n*-heptane,[33] give rise to endothermic effects, having maximum values greater than 1000 J·mol^{-1}, characterized by nearly symmetric curves with respect to the mixture mole fraction; meanwhile, H^E values for mixtures in benzene or tetrachloromethane are considerably lower and became negative, in the whole range of composition or in a part of it, for butane- and pentane-nitriles.

Values at equimolar composition are in the range from (+438 to −112) J·mol^{-1} for benzene-containing mixtures and between (+755 and −31) J·mol^{-1} for mixtures with tetrachloromethane.

The shapes of the experimental curves show a considerable evolution. For butanenitrile or pentanenitrile + tetrachloromethane mixtures the H^E curves are S-shaped. For the pentanenitrile-containing mixture the values range from a maximum of +170 J·mol^{-1} at low nitrile concentration to a minimum of −96 J·mol^{-1} at high nitrile concentration. The x_1 of the positive apex, from the lighter to the heavier nitrile, in benzene are approximately 0.60 and 0.70 for ethane- and propane-nitrile and in tetrachloromethane are 0.43, 0.25, 0.20, and 0.15. The minimum of the curves relative to butane- and pentane-nitrile in benzene are both located around $x_1 = 0.40$.

The combined standard uncertainty of our data for ethanenitrile + benzene is 10 J·mol^{-1}. Most of the values of comparing data, at $x_1 = 0.5$, are within the confidence range (438 ± 10) J·mol^{-1} with the exception of the value due to Fedorova and Sumarokiva.[16] Concerning the ethanenitrile + tetrachloromethane system, the comparison of our value (755 ± 30) J·mol^{-1} and that of Nagata et al.[14] is acceptable. On the other hand, our H^E value at equimolar composition for butanenitrile + benzene (−66 ± 4) J·mol^{-1} seems too negative with respect to the experimental determination of Letcher and Naicker,[23] (−56.9 ± 0.4) J·mol^{-1}.

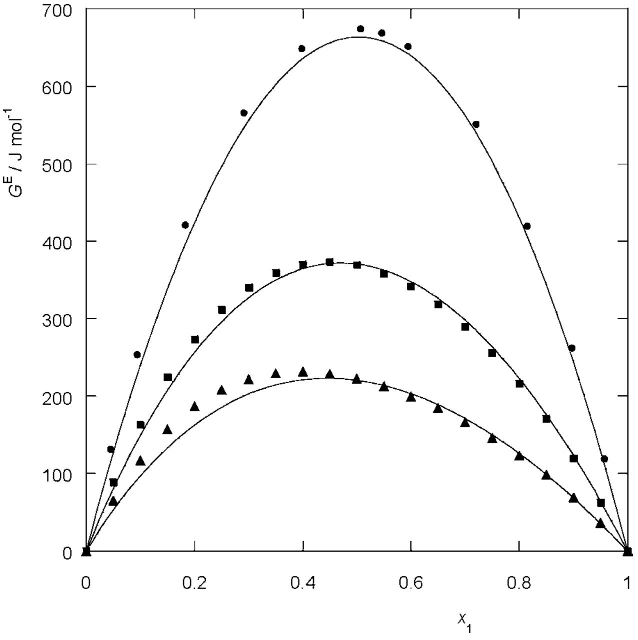

Figure 1. Comparison of theory with experiments for the molar excess Gibbs energies, G^E, at 318.15 K, for alkanenitrile (1) + benzene (2) mixtures versus x_1, the mole fraction of component (1): full lines, DISQUAC predictions; points, experimental results: ●, ethanenitrile, ref 8; ■, propanenitrile, ref 9; ▲, butanenitrile, ref 9.

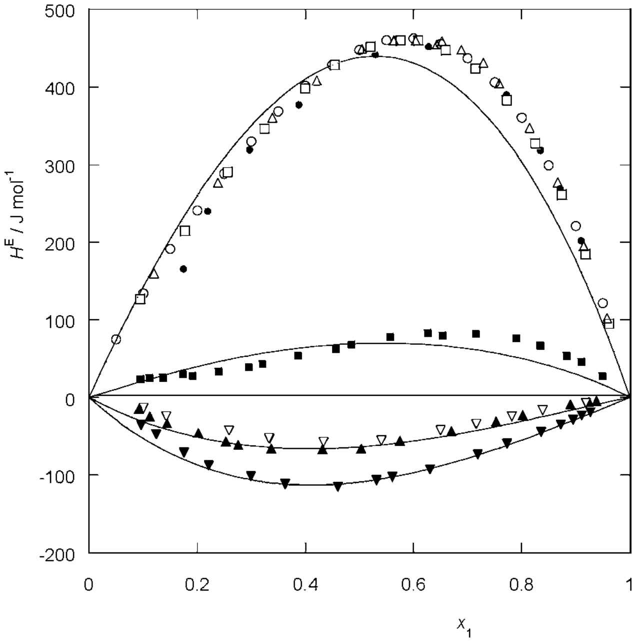

Figure 2. Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for alkanenitrile (1) + benzene (2) mixtures versus x_1, the mole fraction of component (1): full lines, DISQUAC predictions; points, experimental results: ●, ethanenitrile, this work; ○, ethanenitrile ref 10; □, ethanenitrile, ref 11; △, ethanenitrile, ref 12; ■, propanenitrile, this work; ▲, butanenitrile, this work; ▽, butanenitrile, ref 20; ▼, pentanenitrile, this work.

Table 7. Relative Group Increments for Molecular Volumes, $r_G = V_G/V_{CH_4}$, and Areas, $q_G = A_G/A_{CH_4}$, Calculated by Bondi's Method[30] ($V_{CH_4} = 17.12 \cdot 10^{-6}$ m^3·mol^{-1}, $A_{CH_4} = 2.90 \cdot 10^5$ m^2·mol^{-1})

group	r_G	q_G
$-CH_3$	0.79848	0.73103
$-CH_2-$	0.59755	0.46552
$-CN$	0.85862	0.75517

Table 8. Relative Volumes, r_i, Relative Total Surfaces, q_i, and Molecular Surface Fractions, α_{vi}, (v = a, b, r, t) Calculated from the Group Increments r_G and q_G Given in Table 7; a (CH_3, CH_2); r (CN); b (C_6H_6); t (CCl_4)

compound	r_i	q_i	α_{ai}	α_{ri}	α_{bi}	α_{ti}
ethanenitrile	1.6571	1.4862	0.4919	0.5081	0.0000	0.0000
propanenitrile	2.2547	1.9517	0.6131	0.3869	0.0000	0.0000
butanenitrile	2.8522	2.4172	0.6876	0.3124	0.0000	0.0000
pentanenitrile	3.4498	2.8828	0.7380	0.2620	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

Theory

Each class of mixtures under examination, alkanenitrile + benzene and alkanenitrile + tetrachloromethane, is regarded as possessing three types of contact surfaces among the following: type a, aliphatic (CH_3 and CH_2 groups in linear alkanenitriles), type r, nitrile group (CN in alkanenitriles), type b, benzene (C_6H_6), and type t, tetrachlorometane (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[1−3] and need not be repeated here.

The dispersive and the quasi-chemical interchange coefficients, concerning a contact among two different type of surfaces, $C^{dis}_{uv,l}$ and $C^{quac}_{uv,l}$, where u,v = a, b, r, t 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 α_{vi}, of all of 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_{CH_4}, and surface, A_{CH_4}, of methane as unity. Thus, $r_G = V_G/V_{CH_4}$, and $q_G = A_G/A_{CH_4}$. In general, the V_G and A_G values calculated by Bondi[34] 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 nonpolar (type a), polarizable (type b and t), or polar (type r).

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

Each class of mixtures is characterized by three types of contacts; (a,b), (a,r), and (b,r) for mixtures with benzene and (a,r), (a,t), and (t,r) for mixtures with tetrachloromethane. In this work the interchange parameters for the contacts (b,r) and (t,r) have been determined, while the parameters for the remaining contacts were taken from the literature. The rules we found are as follows:

1. Alkanenitrile + Benzene.

1a. (a,b) Contact. DIS. The $C^{dis}_{ab,1}$ dispersive coefficients were assumed constant for every system. The values taken from the literature[35] are: $C^{dis}_{ab,1} = 0.26$ and $C^{dis}_{ab,2} = 0.56$.

1b. (a,r) Contact. DISQUAC. The interchange coefficients, dispersive and quasi-chemical, calculated independently from properties of alkanenitrile + *n*-alkane mixtures can be used.[6] The dispersive coefficients increase with increasing *u*, the total number of carbon atoms in the alkanenitrile (from 2 to 3) and remain constant for $u \geq 3$, $C^{dis}_{ar,1} = 0.40/0.80$ and $C^{dis}_{ar,2} = 0.80/1.70$. The quasi-chemical coefficients decrease as the length of the molecule increases: $C^{quac}_{ar,1}$ values are in the range 6.10 to 5.00, and $C^{quac}_{ar,2}$ values are in the range 7.45 to 5.60.

Table 9. Dispersive and Quasi-Chemical Interchange Energy Coefficients for Contact (b,r) and (t,r) in Linear Alkanenitrile (1) + Benzene or Tetrachloromethane (2) Mixtures; *u* Represents the Total Number of C Atoms in the Alkanenitrile

u	$C^{dis}_{br,1}$	$C^{dis}_{br,2}$	$C^{quac}_{br,1}$	$C^{quac}_{br,2}$	$C^{dis}_{tr,1}$	$C^{dis}_{tr,2}$	$C^{quac}_{tr,1}$	$C^{quac}_{tr,2}$
2	1.05	1.88	2.40	0.10	0.013	0.55	5.50	4.40
3	0.84	1.69	2.40	0.10	0.013[a]	0.45	5.50	4.40
4	0.63	1.44	2.40	0.10	0.013[a]	0.23	5.50	4.40
≥ 5	0.63[a]	1.25	2.40	0.10	0.013[a]	0.010	5.50	4.40

[a] Guessed value.

1c. (b,r) Contact. DISQUAC. All coefficient values concerning the (b,r) contact are collected in Table 9. The dispersive coefficients, $C^{dis}_{br,l}$, show a decreasing trend as the length of the alkyl chain of alkanenitrile increases. The Gibbs energy parameters, $C^{dis}_{br,l}$, values are in the range 1.05 to 0.63. The values of the enthalpic parameters, $C^{dis}_{br,2}$, are between 1.88 for ethanenitrile and 1.25 for 1-pentanenitrile.

The quasi-chemical coefficients, $C^{quac}_{br,1} = 2.40$ and $C^{quac}_{br,2} = 0.10$, are constant and independent of the chain length of the *n*-alkyl groups adjacent to the nitrile group.

2. Alkanenitrile + Tetrachloromethane.

2a. (a,t) Contact. DIS. The $C^{dis}_{at,1}$ dispersive coefficients were assumed constant for every system. The values taken from the literature[36] are: $C^{dis}_{at,1} = 0.093$ and $C^{dis}_{at,2} = 0.18$.

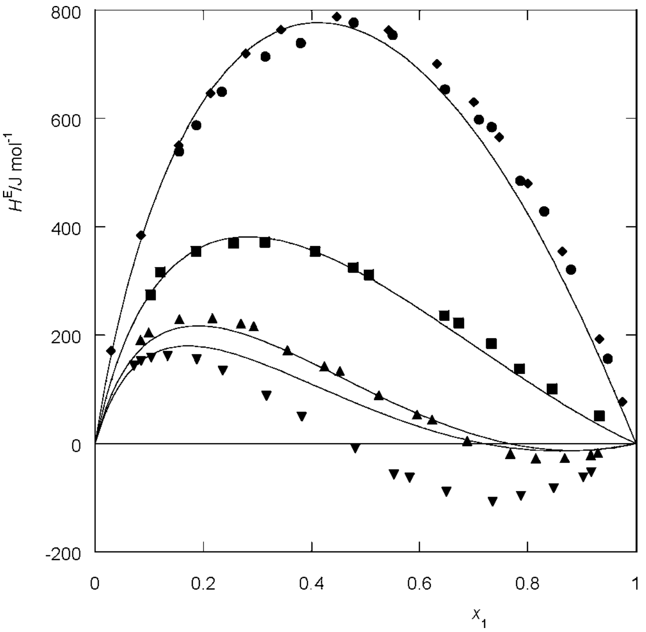

Figure 3. Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for alkanenitrile (1) + tetrachloromethane (2) mixtures versus x_1, the mole fraction of component (1): full lines, DISQUAC predictions; points, experimental results: ●, ethanenitrile, this work; ◆, ethanenitrile, ref 11; ■, propanenitrile, this work; ▲, butanenitrile, this work; ▼, pentanenitrile, this work.

2b. (a,r) Contact. See above, rule 1b.

2c. (t,r) Contact. DISQUAC. All coefficient values concerning the (t,r) contact are presented in Table 9. The dispersive coefficients, $C_{\mathrm{tr,l}}^{\mathrm{dis}}$, shows a decreasing trend as the length of the alkyl chain of alkanenitrile increases. The Gibbs energy parameters, $C_{\mathrm{tr,l}}^{\mathrm{dis}}$, because of the lack of experimental data are estimated as constant value = 0.10. The values of the enthalpic parameters, $C_{\mathrm{tr,2}}^{\mathrm{dis}}$, are between 0.55 for ethanenitrile and 0.010 for pentanenitrile.

The quasi-chemical coefficients, $C_{\mathrm{tr,1}}^{\mathrm{quac}} = 5.50$ and $C_{\mathrm{tr,2}}^{\mathrm{quac}} = 4.40$, are constant and independent of the chain length of the *n*-alkyl groups adjacent to the nitrile group.

Comparison with Experiment and Discussion

Sometimes polar−polar or polar−polarizable group contacts are correctly described by an entirely dispersive approach.[37,38] This is possible when intermolecular forces exerted by the two different groups are similar. In the case of the two classes of mixtures under investigation R-CN + benzene and R-CN + tetrachloromethane, it has been necessary to consider also a quasi-chemical contribution.[7]

The dispersive interchange parameters relative to the nitrile group−benzene or tetrachloromethane exhibit exactly the same trend: they decrease as the length of alkyl group of the nitrile compound increases. The quasi-chemical parameters, $C_{\mathrm{sr,1}}^{\mathrm{quac}}$, where s = b,t, are constant.

The influence of the inductive and steric effect of an alkyl group adjacent to a polar X group (X = CN) on the dispersive and quasi-chemical interchange parameters $C_{\mathrm{sx,l}}^{\mathrm{quac}}$ can be more easily explained if we consider that the interchange energies, $\Delta\varepsilon_{\mathrm{sx}}$, are related to the interaction energies, $\varepsilon_{\mathrm{sx}}$,

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

the ε values being negative.

In polar−polar and polar−polarizable systems the inductive effect exerted by an alkyl group adjacent to the polar X group increases the dispersive interaction energies $\varepsilon_{\mathrm{sx}}$ and consequently decreases $\Delta\varepsilon_{\mathrm{sx}}$ and $C_{\mathrm{sx,l}}^{\mathrm{dis}}$, that is, the dispersive coefficient of the nitrile group or polarizable contact.

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

The systems here considered show moderate deviations from ideality. Indeed, G^{E} at equimolar composition for the mixtures R-CN + benzene are in the range from (+673 to +220) $\mathrm{J\cdot mol^{-1}}$, and for ethanenitrile + tetrachloromethane the value is +1190 $\mathrm{J\cdot mol^{-1}}$; meanwhile H^{E} vary between (+490 and −112) $\mathrm{J\cdot mol^{-1}}$ for R-CN + benzene and in the range from (+913 to −31) $\mathrm{J\cdot mol^{-1}}$ for R-CN + tetrachloromethane. The heat of mixing at 298.15 K at equimolar composition, for each class of mixtures, generally positive, decreases as the length of the alkyl chain of the nitrile compound increases (and became negative in the case of mixtures in benzene of butanenitrile and pentanenitrile and for pentanenitrile + tetrachloromethane).

The few data concerning excess Gibbs energy curves versus x_1 obtained from VLE measurements are satisfactory reproduced. See Figure 1 where reported data refer to ethanenitrile, propanenitrile, and butanenitrile + benzene, at 318.15 K. H^{E} values are generally reproduced quite well by the DISQUAC model. In Figure 2 mixtures containing benzene are considered and in Figure 3 mixtures with tetrachloromethane. The trend of the skew H^{E} curve of pentanenitrile + tetrachloromethane was particularly difficult to reproduce.

From the experimental data reported in Table 1, it is not possible to guess the temperature dependence on G^{E}, for ethanenitrile + benzene. The model predicts a definite increase with T. On the other hand, the experimental results reported in Table 2 show that, for a fixed composition, the H^{E} values increase as T increase; meanwhile, calculated values decrease. The greatest discrepancy is obtained for H^{E} of the ethanenitrile + tetrachloromethane system at 318.15 K.

The temperature dependence of H^{E} (i.e., the excess heat capacity) for R-CN + benzene or tetrachloromethane is not correctly predicted by the DISQUAC model. As a consequence G^{E} values calculated at temperatures different from 298.15 K are not in good agreement with the experimental values. Indeed, the quantities listed in Tables 1 to 3 were calculated with a null value for dispersive and quasichemical heat capacity interchange coefficients, $C_{\mathrm{uv,3}}$. Accordingly, the dispersive contribution to the calculated excess heat capacity is zero, and the quasichemical contribution results from the Boltzmann factor only.

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