Excess Gibbs Free Energies and Excess Volumes of Mixtures Containing Normal Alkanes or Cyclohexane + Thiaalkanes or Dithiaalkanes[†]

Bruno Marongiu,* Gabriele Marras, and Silvia Porcedda

Dipartimento di Scienze Chimiche, Universita' di Cagliari, Via Ospedale 72, 09124 Cagliari, Italy

Stella Dernini

Dipartimento di Ingegneria Chimica e Materiali, Universita' di Cagliari, Piazza D'Armi, 09124 Cagliari, Italy

Vapor-liquid equilibria, by head-space gas-chromatographic analysis of the equilibrated vapor phase directly withdrawn from the equilibration apparatus, and molar excess volumes, V^E, by means of a vibrating-tube densimeter, of binary mixtures containing thiaalkanes or dithiaalkanes with n-alkanes or cyclohexane, were determined at 298.15 K. The excess molar Gibbs free energies, G^E, of the examined mixtures were obtained by a least-squares treatment of the equilibrium data. The G^E and V^E values indicate that the steric effect exerted by the alkyl groups adjacent to the S group causes a regular decrease of the G^E (or V^E) with increasing the number of alkyl groups in the thiaalkane. A tentative approach, based on an additivity scheme of surface interactions combined with the scaled particle theory, is presented to estimate the energies of solvation in terms of group contributions.

Introduction

In continuation of our previous investigations in the field of the thermodynamic properties of liquid organic mixtures, the TOM-Project (*3-5*), undertaken with the purpose of developing accurate group contribution models to be used to predict thermodynamic excess functions, we report here molar excess Gibbs energies, G^E, and molar excess volumes, V^E, at 298.15 K of thiaalkanes, $CH_3(CH_2)_{s-1}S(CH_2)_{t-1}CH_3$, or dithiaalkanes, $CH_3(CH_2)_{s-1}SS(CH_2)_{t-1}CH_3$ (s, t = 1, 2, 3, 4), + heptane or cyclohexane.

The first objective of this study was to extend our previous investigations to a class of technically important compounds, thiaalkanes and dithiaalkanes. The properties of these classes of compounds are of interest in the engineering design of processes connected with fuel desulfurization.

A search of the literature reveals that a single source of excess volumes is available for thiaalkane or dithiaalkane + n-alkane mixtures at 298.15 K (*6-8*); no G^E for mixtures with n-alkane or cyclohexane are available in the literature. To get G^E, we determined the composition of equilibrated vapor by means of head-space gas chromatography (GC), and treated the (x, y) results by a mathematical method similar to that of Barker for (x, P) data (*9*).

The GC technique employed here for obtaining isothermal vapor-liquid equilibria over the whole composition range offers the advantage of being simpler and faster than the conventional static or dynamic methods of measurements. Moreover, in contrast to these latter techniques, the purity of substances is not a critical factor and mixtures with unstable components can be investigated.

The second objective was to investigate orientational effects in thiaalkane and dithiaalkane + n-alkane or cyclohexane mixtures.

The third objective was to get information about the "proximity effect" of S atoms upon molecular interactions and to compare with the behavior of homomorphic oxygen-containing molecules (*4*).

Table I. Experimental Densities, ρ, of the Pure Liquids at 298.15 K

component	ρ/(g cm^{-3})	
	this work	lit.
cyclohexane	0.773 860	0.773 85 (*21*)
heptane	0.679 483	0.679 48 (*21*)
2-thiabutane	0.836 731	0.836 79 (*17*)
3-thiapentane	0.831 141	0.831 18 (*21*)
4-thiaheptane	0.838 579	0.833 2 (*17*)
5-thianonane	0.835 292	
2,3-dithiabutane	1.055 797	1.056 90 (*17*)
3,4-dithiahexane	0.988 002	0.988 18 (*17*)
4,5-dithiaoctane	0.954 863	
5,6-dithiadecane	0.932 904	

Experimental Section

Excess Volumes. Excess volumes were determined from densities, ρ, measured by use of a vibrating-tube densimeter (model DMA 602, Anton Paar) with a precision of $\pm 1.5 \times 10^{-6}$ g cm^{-3} at 298.15 K.

The measuring cell of the apparatus was thermostated with a Heto-Birkerod ultrathermostat to within 0.01 K. The liquid mixtures were prepared by weighing in a septum-capped vial of approximately 5-mL capacity. The two components were injected through the septum into the vial without allowing any vapor to escape, and then the sample was injected into the cell of the densimeter where its density was recorded. The temperature fluctuations in the cell were ± 0.005 K during the course of a run. The mole fraction error is estimated to be less than 1×10^{-4}. The accuracy of the density is estimated to be $\pm 1 \times 10^{-5}$ g cm^{-3}. All liquids were of the best quality available from Fluka (puriss grade).

The estimated purities, as determined by gas-liquid chromatographic analysis, were in all cases better than 98 mol %. The densities of the pure liquids were found to be in good agreement with values published in the literature and are shown in Table I. The excess molar volumes V^E were calculated from the equation

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (1)$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 the molar masses, and ρ_1 and ρ_2 the densities of the two components, and

Table II. Experimental Values of the Molar Excess Volumes, V^E, at 298.15 K for Thiaalkane or Dithiaalkane (1) + Heptane or Cyclohexane (2) Mixtures

x_1	V^E/(cm^3 mol^{-1})	x_1	V^E/(cm^3 mol^{-1})	x_1	V^E/(cm^3 mol^{-1})
2-Thiabutane + Heptane
0.2500	0.3610	0.5125	0.5280	0.5890	0.5100
0.3379	0.4560	0.5245	0.5090	0.6025	0.5120
0.3911	0.5030	0.5365	0.5150	0.7054	0.4860
0.4596	0.5120	0.5455	0.5250	0.8287	0.3710
0.4905	0.5230	0.5545	0.5230	0.8611	0.3030
2-Thiabutane + Cyclohexane
0.1381	0.3830	0.4460	0.6600	0.8549	0.3110
0.2272	0.5090	0.5447	0.6410	0.8561	0.2950
0.3215	0.6130	0.6340	0.5840		
0.3986	0.6500	0.7496	0.4510		
3-Thiapentane + Cyclohexane
0.1225	0.3110	0.4074	0.5650	0.7602	0.3710
0.2065	0.4290	0.5025	0.5630	0.8511	0.2320
0.2889	0.5120	0.6032	0.5130	0.8511	0.2320
0.3225	0.5410	0.7146	0.4270		
4-Thiaheptane + Cyclohexane
0.1502	0.3080	0.3630	0.4800	0.6501	0.3790
0.2337	0.4010	0.4410	0.4890	0.7801	0.2710
0.2914	0.4390	0.4545	0.4790	0.8275	0.2130
0.3421	0.4750	0.5664	0.4520		
5-Thianonane + Cyclohexane
0.0499	0.1230	0.3233	0.4110	0.5818	0.3490
0.0876	0.1990	0.4066	0.4190	0.7175	0.2530
0.1358	0.2800	0.4187	0.4110	0.8754	0.1110
0.2285	0.3730	0.4460	0.4040		
0.2818	0.4020	0.5056	0.3790		
2,3-Dithiabutane + Cyclohexane
0.1614	0.3310	0.3583	0.5520	0.5448	0.5400
0.2380	0.4550	0.3855	0.5640	0.5534	0.5430
0.2985	0.5050	0.4376	0.5620	0.6222	0.4940
0.3577	0.5550	0.4745	0.5650	0.7517	0.3610
3,4-Dithiahexane + Cyclohexane
0.1301	0.1950	0.4703	0.3240	0.7776	0.1810
0.2624	0.3010	0.5705	0.2990	0.8995	0.0710
0.3729	0.3330	0.6362	0.2620		
0.4184	0.3290	0.7001	0.2210		
4,5-Dithiaoctane + Cyclohexane
0.1230	0.1620	0.3188	0.2530	0.5253	0.2270
0.1891	0.1930	0.4098	0.2470	0.6351	0.1790
0.3134	0.2550	0.4182	0.2510	0.8024	0.1010
5,6-Dithiadecane + Heptane
0.1703	−0.2310	0.3697	−0.3530	0.6021	−0.3240
0.2768	−0.2980	0.4328	−0.3620	0.7125	−0.2710
0.3594	−0.3490	0.5310	−0.3490	0.7878	−0.2180
5,6-Dithiadecane + Cyclohexane
0.2052	0.1980	0.3589	0.2370	0.5316	0.2010
0.2634	0.2270	0.4065	0.2280	0.6115	0.1740
0.3194	0.2310	0.4551	0.2240	0.6370	0.1760
0.3312	0.2310	0.4992	0.2130	0.7124	0.1170

ρ is the density of the mixture. The V^E values were accurate to ± 0.003 cm^3 mol^{-1}.

The equation used to express the composition dependence of V^E was

$$V^E_{calc}/(cm^3\ mol^{-1}) = x_1 x_2 \sum_{i=0}^{3} a_i (x_1 - x_2)^i \qquad (2)$$

The experimental values of the excess volumes for the thiaalkanes or dithiaalkanes + heptane or cyclohexane mixtures are reported in Table II and plotted in Figures 1 and 2.

The coefficients a_i are listed in Table III along with the standard deviations $\sigma(V^E)$:

$$\sigma(V^E) = [\sum (V^E_{calc} - V^E)^2/(N - n)]^{1/2} \qquad (3)$$

where N is the number of experimental points and n is the number of coefficients a_i.
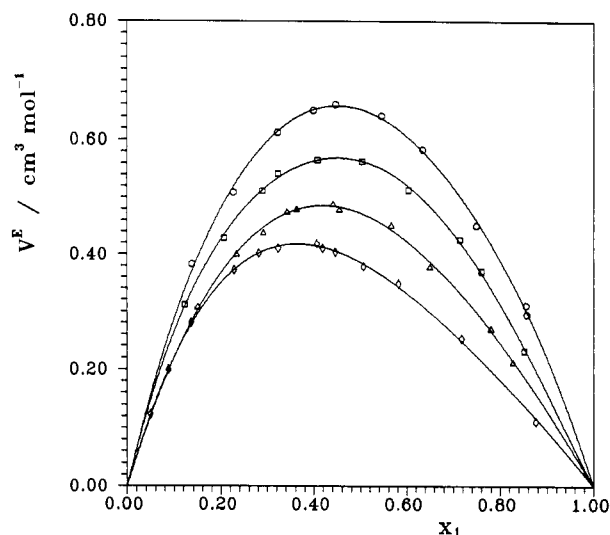

Figure 1. Excess molar volumes, V^E, vs x_1 for thiaalkane (1) + cyclohexane (2) mixtures at 298.15 K: O, 2-thiabutane; □, 2-thiapentane, △, 2-thiaheptane, ◊, 2-thianonane.
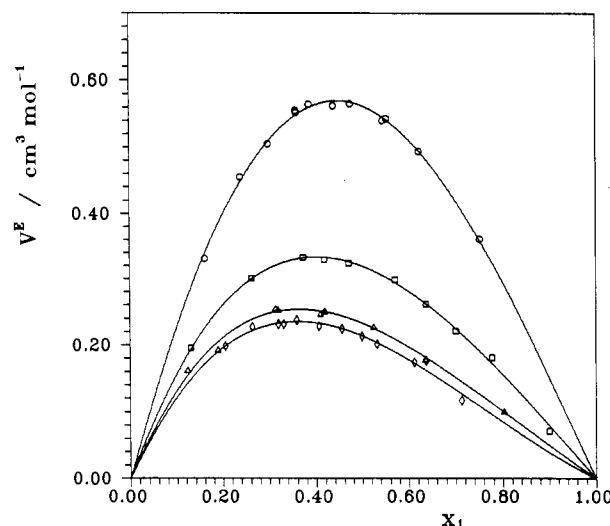

Figure 2. Excess molar volumes, V^E, vs x_1 for dithiaalkane (1) + cyclohexane (2) mixtures at 298.15 K: O, 2,3-dithiabutane, □, 3,4-dithiahexane; △, 4,5-dithiaoctane; ◊; 5,6-dithiadecane.

Table III. Parameters a_i of the Best Fitting Equation for Molar Excess Volume, V^E, at 298.15 K, Equation 2, and Standard Deviations $\sigma(V^E)$, Equation 3, for Thiaalkane or Dithiaalkane (1) + Heptane or Cyclohexane (2) Mixtures[a]

thiaalkane	m	a_0	a_1	a_2	a_3	σ/(cm^3 mol^{-1})
2-thiabutane	7	2.0752	0.3597	0.4901		0.012
2-thiabutane	c-6	2.6070	−0.4740	0.3241		0.008
3-thiapentane	c-6	2.2560	−0.4132	0.1553	−0.5015	0.006
4-thiaheptane	c-6	1.8901	−0.6362	−0.0710		0.006
5-thianonane	c-6	1.5456	−0.8733	0.3236		0.004
2,3-dithiabutane	c-6	2.2491	−0.5421	−0.2265		0.006
3,4-dithiahexane	c-6	1.2781	−0.5437	0.0572		0.006
4,5-dithiaoctane	c-6	0.9305	−0.5728	0.1225		0.007
5,6-dithiadecane	7	−1.4237	0.2562	−0.0414		0.006
5,6-dithiadecane	c-6	0.8536	−0.5779	0.0616		0.006

[a] m is the number of C atoms in the alkane; c-6 means cyclohexane.

Liquid–Vapor Equilibria. The (x, y) data were obtained with a gas-chromatographic technique in which an equilibration cell was combined with a gas chromatograph (Carlo Erba Model HRGC 5300) for the analysis of the gas phase (air + vapor) at atmospheric pressure. The apparatus, assembled in our labo-

Table IV. Vapor Pressures $P_i°$, Molar Volumes $V_i°$, and Second Molar Virial Coefficients B_{ii} for Pure Compounds at 298.15 K and Cross Virial Coefficient B_{ij}

compound	$P_i°$ [a]/kPa	$V_i°$ [b]/(cm^3 mol^{-1})	$-B_{ii}$/(cm^3 mol^{-1})	$-B_{ij}^{d,e}$/(cm^3 mol^{-1})	$-B_{ij}^{d,f}$ (cm^3 mol^{-1})
heptane	6.09	147.70	3018		
cyclohexane	13.01	108.75	1874		
2-thiabutane	21.32	90.99	1560	1910	1600
3-thiapentane	7.78	107.58	2250	2400	1910
4-thiaheptane	0.86	141.93	3600^g	3300^g	2610^g
2,3-dithiabutane	3.82	89.13	1900	2450	1960
3,4-dithiahexane	0.56	123.72	4500	3520	2600
4,5-dithiaoctane	0.07	157.41	7200^g	4360^g	3500^g
5,6-dithiadecane	0.01^c	190.92	9800^g	5210^g	4200^g
nitrogen			0000		100^h

^{a} References 16 and 17. ^{b} Reference 21. ^{c} Extrapoled. ^{d} Computed according to Hayden and O'Connell (*19*). ^{e} Refers to Mixtres with cyclohexane. ^{f} Refers to mixture with *n*-heptane. ^{g} Estimated from B_{ii} values of a related compound (*20*). ^{h} The same value applies for all mixtures of nitrogen with the listed substances.

ratory, and the procedure were described in detail in a previous paper (*10*). A capillary column (poly(methylphenylsiloxane)) was used for the analysis.

All chemicals were products from Fluka of the best quality grade. They were used without further purification, and their purities, as checked by gas-chromatographic analysis, were >98 mol%. All mixtures were prepared by weighing. The correction for evaporation of constituents was estimated to be less than 0.05% of the lowest liquid mole fraction x_i and has been neglected.

The values of mole fraction y_1 in the vapor phase (the subscript 1 indicates thiaalkane) were obtained from

$$y_1 = \frac{1}{1 + r_f(A_2/A_1)} \quad (4)$$

where A_1/A_2 is the measured peak area ratio of the two components and r_f the response factor of the chromatograph for the mixtures under examination. The overall uncertainty in y_1, resulting from the uncertainty in A_1/A_2, was generally less than 1% of the lowest y_1.

The values of r_f for each mixture were determined, by calibration analysis, through the equation

$$r_f = \frac{A_1°/A_2°}{P_1°/P_2°} \quad (5)$$

where $A_1°/A_2°$ is the area ratio of the peaks obtained when a vapor of pure components ($P_1°/P_2°$ is the pure component vapor pressure ratio) is injected into the chromatograph under the same conditions as for the unknown samples. We carried out a number of r_f determinations by injecting equal volumes of the two vapors equilibrated with the pure liquids at 298.15 K.

A possible dependence of r_f on composition as well as on the quantity injected, if any, was in any case below the experimental uncertainty (1.5%).

The reliability of the apparatus and procedure was checked by carrying out measurements on the test mixture ethanol + cyclohexane over the entire composition range.

Data Analysis

The experimental values of γ_1/γ_2, the ratio of the activity coefficients of the constituents, were used in a nonlinear least-squares procedure, similar to that described by Barker (*9*) for treatment of x–total pressure data. In our case, the sum σ of the squares of residuals extended over all n experimental points to be minimized is

$$\sigma = \sum_{i=1}^{n} (\ln(\gamma_1/\gamma_2)_{i,\text{exp}} - \ln(\gamma_1/\gamma_2)_{i,\text{calc}})^2 \quad (6)$$

the experimental γ_1/γ_2 ratio being given by

$$\left(\frac{\gamma_1}{\gamma_2}\right)_{\text{exp}} = \left(\frac{x_2}{x_1}\right)\left(\frac{A_1}{A_2}\right)\left(\frac{w_1}{w_2}\right)\left(\frac{P_2°}{P_1°}\right)\left(\frac{1}{r_f}\right) \quad (7)$$

The parameters of the function representing the activity

coefficients in $(\gamma_1/\gamma_2)_{\text{calc}}$ are determined together with the product $(P_2°/P_1°)(1/r_f)$, treated as an adjustable parameter.

In eq 7 w_i is a factor relevant to vapor-phase nonideality, which is calculated in terms of the molar second virial coefficients B_{ii} and B_{ij} taking into account also the presence of air in the vapor phase.

In Table IV are collected the values of the quantities $V_i°$, $P_i°$, B_{ii}, and B_{ij} used in evaluating w_i. Although most B_{ii} and B_{ij} are estimated values and affected by large uncertainties, the w_i terms differ from 1 by less than 2% and partially compensate in the ratio w_1/w_2, eq 7. The maximum deviations of y_1, γ_i, and G^E from the values calculated with $w_1 = w_2 = 1$ (that is, neglecting vapor-phase nonideality) were 0.001, 2% and 5 J mol^{-1}, respectively.

Results

The experimental x_1 and A_1/A_2 together with the calculated values of y_1 and G^E are collected in Table V, while Table VI gives the a_i values of the Redlich-Kister equation ($i, j = 1, 2; i \neq j$) (*12*)

$$\ln \gamma_i = [a_0 - 3(-1)^j a_1 + 5a_2]x_j^2 +$$
$$4(-1)^j[a_1 - 4(-1)^j a_2]x_j^3 + 12a_2 x_j^4 \quad (8)$$

which was found convenient to represent activity coefficients in eq 6. This table also lists the values of r_f obtained from the fitting as well as the standard deviation for the representation of $\ln(\gamma_1/\gamma_2)$.

In Figure 3 the plot of $\ln(\gamma_1/\gamma_2)$ is shown for the system 2-thiabutane + heptane. In Figures 4 and 5 is illustrated the behavior of the excess molar Gibbs energy, G^E, for all the systems investigated. The G^E curves were computed from the coefficients a_i in eq 8 through the equation

$$G^E/RT = x_1 x_2 \sum_{i=0}^{i=2} a_i(x_2 - x_1)^i \quad (9)$$

All mixtures exhibit positive deviations, and the G^E curves are slightly asymmetrical.

Discussion

The first point worth noting is that *n*-thiaalkane + *n*-alkane mixtures are more endothermic than the corresponding homomorphic *n*-ether + *n*-alkane mixtures (*4*). The difference in dipole moments between thiaalkanes ($\simeq 1.6$ D) and ethers ($\simeq 1.2$ D) is not sufficient to explain the differences in G^E and V^E which are probably due mainly to stronger dispersive interactions between S atoms than O atoms. Comparison of different characteristic properties of homomorphic R_2X compounds, where $X = CH_2$, O, or S (Table VII), gives indications concerning the relative strength of interaction

Table V. Experimental Values of the Liquid-Phase Mole Fraction x_1, Chromatographic Peak Area Ratios of Vapors A_1/A_2, and Calculated Excess Molar Gibbs Energies G^E at 298.15 K

x_1	A_1/A_2	G^E/(J mol^{-1})	x_1	A_1/A_2	G^E/(J mol^{-1})	x_1	A_1/A_2	G^E/(J mol^{-1})	x_1	A_1/A_2	G^E/(J mol^{-1})
					2-Thiabutane (1) + Heptane (2)						
0.1172	0.2225	112	0.3983	0.8913	286	0.7140	2.4328	274	0.9337	10.0880	92
0.2002	0.3955	180	0.5342	1.3657	311	0.7824	3.2796	236			
0.3473	0.7451	267	0.5929	1.6290	308	0.8693	5.2129	164			
					2-Thiabutane (1) + Cyclohexane (2)						
0.1085	0.1426	153	0.3909	0.5750	351	0.7099	1.4191	293			
0.2262	0.3025	256	0.5325	0.8281	370	0.8078	2.2537	214			
0.3691	0.5370	342	0.6192	1.0484	345	0.9213	5.7548	101			
					3-Thiapentane (1) + Heptane (2)						
0.0577	0.0603	59	0.2010	0.2236	178	0.5290	0.7343	297	0.8131	2.1760	193
0.1029	0.1103	101	0.3286	0.3950	252	0.6079	0.9539	288	0.8838	3.5401	135
0.1627	0.1760	150	0.4106	0.5272	282	0.0682	1.3285	259			
					3-Thiapentane (1) + Cyclohexane (2)						
0.1024	0.0747	119	0.4150	0.3494	316	0.6907	0.8046	269			
0.2140	0.1620	213	0.4941	0.4310	326	0.7935	1.2763	204			
0.3195	0.2564	279	0.5728	0.5390	316	0.9035	2.8372	114			
					4-Thiaheptane (1) + Heptane (2)						
0.0811	0.0220	60	0.4087	0.1385	204	0.5592	0.2290	205	0.8805	1.0894	91
0.1218	0.0345	88	0.4637	0.1668	209	0.6375	0.3017	191			
0.1972	0.0575	132	0.5074	0.1932	209	0.7147	0.4086	169			
0.2727	0.0827	168	0.5144	0.1978	209	0.7829	0.5800	142			
					4-Thiaheptane (1) + Cyclohexane (2)						
0.1794	0.0400	161	0.4150	0.1050	236	0.7054	0.2910	180	0.8598	0.6930	103
0.2303	0.0520	187	0.4810	0.1300	236	0.7737	0.4040	149			
0.3152	0.0740	219	0.6370	0.2220	205	0.8261	0.5460	122			
					2,3-Dithiabutane (1) + Heptane (2)						
0.1582	0.0620	264	0.3982	0.1557	522	0.7175	0.3270	505	0.9226	0.8900	193
0.1983	0.0772	321	0.4714	0.1878	559	0.7790	0.3895	440			
0.3002	0.1179	441	0.5916	0.2457	570	0.8538	0.5300	329			
					2,3-Dithiabutane (1) + Cyclohexane (2)						
0.1610	0.0440	327	0.3887	0.0890	595	0.6776	0.1660	551			
0.2482	0.0630	463	0.4907	0.1110	626	0.7543	0.2050	468			
0.3329	0.0790	555	0.6064	0.1410	600	0.8941	0.4200	233			
					3,4-Dithiahexane (1) + Heptane (2)						
0.1544	0.0216	216	0.3897	0.0574	381	0.6398	0.1144	373	0.8513	0.2800	202
0.2504	0.0352	302	0.4604	0.0703	400	0.6858	0.1320	348			
0.3209	0.0458	349	0.5615	0.0919	398	0.7831	0.1921	273			
					3,4-Dithiahexane (1) + Cyclohexane (2)						
0.1627	0.0181	262	0.3415	0.0358	413	0.7202	0.1052	335			
0.2193	0.0237	324	0.5565	0.0627	428	0.8024	0.1524	258			
0.2727	0.0288	371	0.6533	0.0841	383	0.9146	0.3572	124			
					4,5-Dithiaoctane (1) + Heptane (2)						
0.1201	0.0095	135	0.3901	0.0336	277	0.7379	0.1097	214			
0.2057	0.0163	200	0.5548	0.0568	280	0.8028	0.1510	175			
0.2921	0.0239	246	0.6694	0.0829	247	0.8796	0.2538	117			

Table VI. Parameters a_i of the Best Fitting Equation for (x, y) at 298.15 K, Standard Deviations σ, and Chromatographic Response Factor, r_f, Determined by the Least-Squares Procedure[a]

thiaalkane	m	a_0	a_1	a_2	$r_f{}^b$	σ/(J mol^{-1})
2-thiabutane	7	0.4978	0.0844	0.0359	0.34	0.006
2-thiabutane	c-6	0.6011	−0.0022	−0.1628	0.47	0.002
3-thiapentane	7	0.4779	0.0446	−0.0204	0.53	0.008
3-thiapentane	c-6	0.5252	−0.0168	−0.1149	0.74	0.004
4-thiaheptane	7	0.3378	−0.0180	−0.0048	1.33	0.007
4-thiaheptane	c-6	0.3782	−0.0777	0.0067	2.15	0.003
2,3-dithiabutane	7	0.9157	0.1880	0.0481	0.28	0.003
2,3-dithiabutane	c-6	1.0100	0.0091	−0.0416	0.36	0.002
3,4-dithiahexane	7	0.6507	0.0178	−0.0175	0.84	0.001
3,4-dithiahexane	c-6	0.7108	−0.0961	0.0004	1.31	0.003
4,5-dithiaoctane	7	0.4618	−0.0369	0.0078	4.22	0.003

[a] m is the number of C atoms in the alkane; c-6 means cyclohexane. [b] Values of the experimental r_f, eq 5.

forces between X groups. The force field of the CH$_2$ group appears to be somewhat stronger than the dispersive force field of the isoelectronic O atom but much weaker than the force field of the more electron rich S atom.

Comparison of dithiaalkanes with monothiaalkanes reveals a considerable decrease of the intermolecular forces between RSSR molecules and the solvent when two atoms of S are directly linked: in fact the G^E and V^E values of RSSR are lower than those of the corresponding hypothetical molecule in which the two S groups interact in an independent way.

Table VIII gives the values of the activity coefficients at infinite dilution, $\gamma_i{}^\infty$, obtained from the parameters of eq 8, as well as the molar Gibbs energies of solvation, $\Delta G^\circ{}_{\text{solv},i}$, of component i. These were calculated from the following equation:

$$\Delta G^\circ{}_{\text{solv},i} = RT \ln \gamma_i{}^\infty + RT \ln(P_i{}^\circ V_j{}^\circ/RT) \qquad (10)$$

where $V_j{}^\circ$ is the molar volume of the solvent.

The $\Delta G^\circ{}_{\text{solv},i}$ values of thiaalkanes and dithiaalkanes in various solvents can be reproduced by a simple scheme of surface group contributions, presented in previous works (10, 13) in which the molecules are subdivided into surface groups, S, each of which is assumed to contribute a constant amount, B_s, to $\Delta G^\circ{}_{\text{solv},i}$ (Table IX).

In order to have an estimate of the importance of the solute–solvent interactions in determining the group contribution

Table VII. Molar Volumes, Molar Enthalpies of Vaporisation, ΔH_{vap}, Second Molar Virial Coefficients, B_{11}, and Solubility Parameters, δ, at 298.15 K of Homomorphic n-Alkanes, n-Ethers, and n-Thiaalkanes

| R₂X	$V^a/(10^{-6}$ m³ mol⁻¹)	$\Delta H_{vap}{}^b/(10^3$ J mol⁻¹)	$B_{11}{}^c/(10^{-6}$ m³ mol⁻¹)	$\delta^d/(10^3$ J^{1/2} m^{-3/2})
(C₂H₅)₂CH₂	116.10	26.43	-1195	14.5
(C₂H₅)₂O	104.75	27.24	-1165	15.4
(C₂H₅)₂S	107.58	35.77	-2250	17.5
(C₃H₇)₂CH₂	147.48	36.60	-3018	15.2
(C₃H₇)₂O	137.72	35.69		15.5
(C₃H₇)₂S	141.93	44.52	-3600	17.2

^{a} References 16 and 17. ^{b} Reference 21. ^{c} References 16 and 17. ^{d} $\delta = ((\Delta H_{vap} - RT)/v)^{1/2}$.
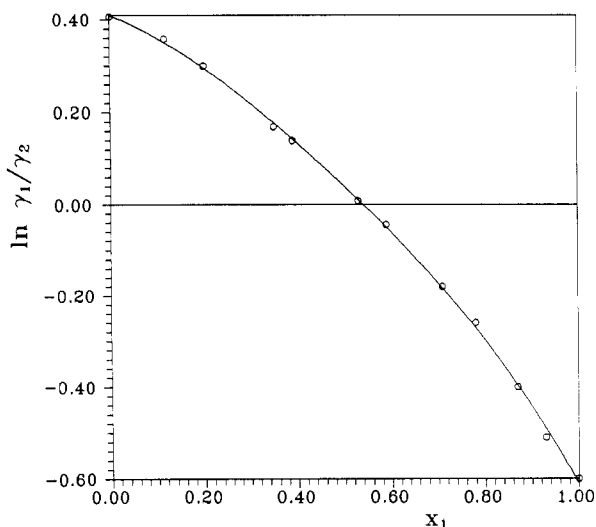
Figure 3. $\ln (\gamma_1/\gamma_2)$ vs x_1 for 2-thiabutane + n-heptane mixtures at 298.15 K: points, experimental results; full lines, best fitting of our results.
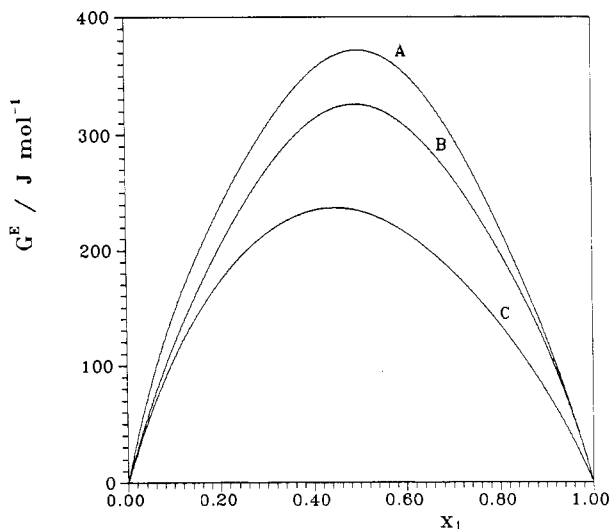
Figure 4. Excess molar Gibbs energies, G^E, vs x_1 for thiaalkane (1) + cyclohexane (2) mixtures at 298.15 K: A, 2-thiabutane; B, 3-thiapentane; C, 4-thiaheptane.

values calculated above, we have applied the scaled particle theory (14) to our system. According to this theory, the molar Gibbs energy of solvation is given by

$$\Delta G^{\circ}{}_{solv,i} = G_c + \Delta G_{int} \qquad (11)$$

where G_c is the free energy spent for the creation of the cavity in the solvent to accomodate the solute and ΔG_{int} is the Gibbs energy of the solute–solvent interaction. The expression for
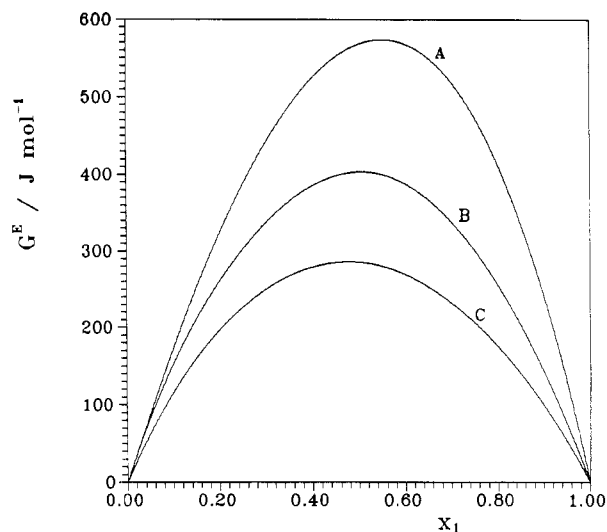
Figure 5. Excess molar Gibbs energies, G^E, vs x_1 for dithiaalkane (1) + heptane (2) mixtures at 298.15 K: A, 2,3-dithiabutane; B, 3,4-dithiahexane; C, 4,5-dithiaoctane.

Table VIII. Activity Coefficients at Infinite Dilution, $\gamma_i{}^\infty$, and Molar Gibbs Energies of Solvation, $\Delta G^{\circ}{}_{solv,i}$, of the Components of Binary Mixtures at 298.15 K^{a,b}

thiaalkane	m	$\gamma_1{}^\infty$	$-\Delta G^{\circ}{}_{solv,1}/(kJ$ mol⁻¹)	$\gamma_2{}^\infty$	$-\Delta G^{\circ}{}_{solv,2}/(kJ$ mol⁻¹)
2-thiabutane	7	1.50	15.53	1.85	19.31
2-thiabutane	c-6	2.17	15.37	1.83	17.46
3-thiapentane	7	1.56	17.93	1.78	19.00
3-thiapentane	c-6	1.77	18.37	1.81	17.07
4-thiaheptane	7	1.37	23.71	1.47	18.78
4-thiaheptane	c-6	1.68	23.96	1.45	16.93
2,3-dithiabutane	7	2.09	18.97	3.05	18.12
2,3-dithiabutane	c-6	2.32	19.46	2.50	16.74
3,4-dithiahexane	7	2.10	23.72	1.90	18.48
3,4-dithiahexane	c-6	2.24	24.31	1.89	16.62
4,5-dithiaoctane	7	1.76	29.31	1.59	18.33

^{a} m is the number of C atoms in the alkane; c-6 means cyclohexane. ^{b} $\Delta G^{\circ}{}_{solv}$ refers to the transfer process [component (ideal gas, 1 mol dm1⁻³) = component (solute obeying Henry's law, 1 mol dm⁻¹)] and is calculated from eq 10. The value for the standard process [component (ideal gas, 101.325 kPa) = component (solute obeying Henry's law, at unit mole fraction)] can be calculated as $\Delta G^{\circ}{}_{solv} = RT \ln(\gamma)_i{}^\infty P^{\circ}/101.325$).

Table IX. Group Contribution, B_s, to the Gibbs Energy of Solvation of Thiaalkanes and Dithialkanes in Organic Solvents at 298.15 K

solvent group	B_s (kJ mol⁻¹) C₇H₃₁₆	C₆H₁₂	solvent group	B_s (kJ mol⁻¹) C₇H₁₆	C₆H₁₂
CH₂	-3.1	-3.0	SS	-13.0	-13.6
CH₃	-4.9	-4.7	A	5.4	4.7
S	-6.9	-7.7			

G_c is given elsewhere (14). The required solvent densities were measured or found in the literature; the hard-sphere diameter for each solute and solvent was assumed to be equal to the van der Waals volume of the compound calculated according to Bondi's method (15). The result of these calculations shows that G_c is practically linear with the surface area or volume of the solute molecule for the size range of the compounds considered here. This implies that the contribution to G_c is similar for groups of similar dimensions: the value of the S group is about 2.6 kJ mol⁻¹, that of the CH₂ group is 2.5 kJ mol⁻¹, and that of the CO group is 3.0 kJ mol⁻¹ (13). The observed negative values of the group contributions to the experimental $\Delta G^{\circ}{}_{solv,i}$ values are, in this model, determined by the solute–solvent interactions, which carry an opposite and larger in absolute value contribution with

respect to the Gibbs energy of cavitation. From eq 11 the following values have been calculated: $\Delta G_{int}(CH_2) = -5.6$ kJ mol^{-1} and $\Delta G_{int}(S) = -9.5$ kJ mol^{-1}.

The contribution to $\Delta G°_{solv,i}$ from the SS group seems to be less negative than the contribution from two separate S groups. The interaction of the two adjacent S groups lowers the effect of a single S group on $\Delta G°_{solv,i}$.

List of Symbols

A_i	peak area of component i in the vapor phase
B_{ij}	second virial coefficient ($i, j = 1, 2$)
a_i	coefficient of eqs 2 and 8
γ_i	activity coefficient of component i
γ_i^∞	activity coefficient of component i at infinite dilution
G_c	Gibbs energy of cavitation
G^E	excess Gibbs energy
$\Delta G°_{solv}$	Gibbs energy of solvation
ΔG_{int}	Gibbs energy of the solute–solvent interaction
P	pressure
$P_i°$	vapor pressure of pure liquid i
r_f	response factor of the gas chromatograph for a pair of components
T	temperature (K)
$V_i°$	molar volume of pure liquid i
x_i	molar fraction in the liquid phase
y_i	molar fraction in the vapor phase
ρ	molar density
σ	standard deviation of the fit of $\ln(\gamma_1/\gamma_2)$ or V^E
w_i	vapor-phase nonideality factor of i

Literature Cited

(1) Kehiaian, H. V. *Ber. Bunsen-Ges. Phys. Chem.* **1977**, *81*, 908.

(2) Kehiaian, H. V. *Pure Appl. Chem.* **1985**, *57*, 15.

(3) Kehiaian, H. V.; Marongiu, B. *Fluid Phase Equilib.* **1988**, *40*, 23.

(4) Kehiaian, H. V.; Tine, M. R.; Lepori, L.; Matteoli, E.; Marongiu, B. *Fluid Phase Equilib.* **1989**, *46*, 131.

(5) Marongiu, B.; Kehiaian, H. V. *Thermochim. Acta* **1987**, *122*, 45.

(6) Ferhad-Hamida, Z.; Philippe, R.; Merlin, J. C.; Kehiaian, H. V. *J. Chim. Phys. Phys.-Chim. Biol.* **1975**, *72*, 935.

(7) Ferhad-Hamida, Z.; Philippe, R.; Merlin, J. C.; Kehiaian, H. V. *J. Chim. Phys.* **1979**, *76*, 130; *Int. DATA Ser., Sel. Data Mixtures* **1977**, *2*, 120.

(8) Ferhad-Hamida, Z.; Philippe, R.; Merlin, J. C.; Kehiaian, H. V. *J. Chim. Phys. Phys.-Chim. Biol.* **1980**, *77*, 445; *Int. DATA Ser., Sel. Data Mixtures* **1978**, *2*, 110.

(9) Barker, J. A. *Aust. J. Chem.* **1953**, *6*, 207.

(10) Marongiu, B.; Monaci, R.; Porcedda, S. *Fluid Phase Equilib.* **1993**, *84*, 281.

(11) Cancellu, D.; Marongiu, B.; Porcedda, S. *Thermochim. Acta* **1991**, *178*, 33.

(12) Prausnitz, J. M. *Molecular Thermodynamics of Fluid Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1969.

(13) Giannotti, A.; Lepori, L.; Matteoli, E.; Marongiu, B. *Fluid Phase Equilib.* **1991**, *65*, 275.

(14) Pierotti, R. A. *Chem. Rev.* **1976**, *76*, 717.

(15) Bondi, A. *Physical Properties of Molecular Crystal, Liquids and Glasses*; John Wiley & Sons: New York, 1968.

(16) *TRC, Thermodynamic Tables Hydrocarbons*; Thermodynamic Research Center: College Station, TX.

(17) *TRC, Thermodynamic Tables Non-Hydrocarbons*; Thermodynamic Research Center: College Station, TX.

(18) White, P. T.; Barnard-Smith, D. G.; Fidler, F. A. *Ind. Eng. Chem.* **1952**, *44*, 1430.

(19) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.

(20) Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures. A Critical Compilation*; Clarendon Press: Oxford, 1980.

(21) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*; John Wiley & Sons: New York, 1986.