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Liquid-Vapor Equilibria in Mixtures of Carbon Tetrachloride and Chloroform with Dimethyl Sulfide and Diethyl Sulfide

Donald F. Gray, Neil F. Pasco, and Arthur G. Williamson*

Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

Vapor pressures at 298.15 K and the excess Gibbs energies derived therefrom are reported for mixtures of carbon tetrachloride + dimethyl sulfide, carbon tetrachloride + diethyl sulfide, chloroform + dimethyl sulfide, and chloroform + diethyl sulfide. All four systems show negative deviations from ideality. The especially large deviations in the chloroform systems are interpreted in terms of hydrogen bonding.

Introduction

The studies reported here parallel earlier work (*1–5*) on binary mixtures of di-*n*-alkyl ethers with carbon tetrachloride and with chloroform and complement measurements already reported (*5*, *6*) of other properties of mixtures of di-*n*-alkyl sulfides with carbon tetrachloride with chloroform. Among other things these results can be used to extend the data base for mixture property prediction provided by UNIFAC (*7*) to include an additional structural group CH_2S analogous to the CH_2O group used by Fredenslund et al. for the ethers.

Materials

Carbon tetrachloride and chloroform were purified as described by Beath and Williamson (*1*, *3*). The alkyl sulfides were purified as described by Gray and Williamson (*6*). All four compounds were examined by gas–liquid chromatography on a 2-m column of 5% SE 30 and gave only one peak. No measurable changes (less than 0.05 mmHg) in vapor pressure were observed on isothermal distillation of up to 70% of a sample of each pure compound.

Experimental Section

The total vapor pressures of mixtures of known overall composition were measured by using the static method and apparatus described by Bissell and Williamson (*4*). The temperature scale used in this work was established by calibrating an 11-junction copper–constantan thermocouple against the vapor pressure of carbon tetrachloride using the published data of Marsh (*8*). Pressures were measured on a 20-mm-bore mercury manometer with a Wild cathetometer and are believed to be accurate to ±(5–25) Pa including any uncertainty in temperature from measurement to measurement.

Results

Vapor pressures of the pure compounds are shown in Table I where they are compared with published data. Table II shows the values of the physical properties of the pure compounds used in calculating the vapor-phase fugacities and subsequently the excess Gibbs energies from the measurements on the mixtures. The raw measurements on the mixtures are recorded in Table II in which the first two columns give the amounts of each component present in the vapor pressure cell (whose total volume was 143 ± 1 cm³) and the third column gives the measured vapor pressure. From these data compositions of the phases in equilibrium the excess Gibbs energy were calculated by a modification (*4*) of Barker's (*9*) procedure which gives the parameters g_n in the equation (*11*)

$$G^E/RT = x(1-x)\sum_{n=0}^{m} g_n(1-2x)^n \tag{1}$$

where x is the mole fraction of halocarbon.

Table I. Physical Properties of Pure Substances at 25 °C

compound	vap press./Pa	liq vol/ cm³ mol⁻¹	second virial coeff/ cm³ mol⁻¹
carbon tetrachloride	15 227 ± 3[a] (*8*)	97.1[a] (*12*)	−1605[a] (*13*)
chloroform	26 254 ± 5[a] 26 217 ± 34[a] (*4*) 26 241 ± 25[a] (*10*)	80.7[a] (*12*)	−1115[a] (*13*)
dimethyl sulfide	64 320 ± 25[a]	73.8[a] (*12*)	−904[a] (*13*)
diethyl sulfide	7 852 ± 4[a]	108.5[a] (*12*)	−2204[a] (*13*)

[a] Used in analysis of our results. Where no reference is given, the figures are for properties measured in this study.

Table II also shows the liquid and vapor compositions for each run, the observed vapor pressure, and the differences between the measured vapor pressures and those computed by using activity coefficients derived from eq 1 with the parameters given in Table III. The values of the parameters in eq 1 for the various mixtures are shown in Table III along with the values of σ defined by the relation

$$\sigma = [\sum(p_{\text{exptl}} - p_{\text{calcd}})^2/(N-m)]^{1/2} \tag{2}$$

where N is the number of experimental points and m is the number of parameters. In each case the number of parameters is that which minimizes σ. The excess Gibbs energies generated from eq 1 with the parameters of Table III are shown in Figure 1.

Discussion

The excess properties of the mixtures of dialkyl sulfides with either carbon tetrachloride or chloroform are similar in sign and magnitude to those for the corresponding ether mixtures and suggest similar relatively strong interactions. Hydrogen-bond formation between sulfides and chloroform has been confirmed by NMR spectroscopy by Jolley et al. (*4*).

Earlier measurements on binary mixtures of ethers, hydrocarbons, and chlorocarbons were interpreted (*4*) by using relations based on the quasi-lattice treatment of Barker (*15*) and although reasonably good correlations could be obtained among the systems for which data had been used in fitting the equations, extrapolation to other systems with the same interacting groups in different configurations was not then regarded as successful.

The later development of the UNIFAC method by Fredenslund et al. (*7*) revived our interest in group contribution correlations. For this reason we have used Fredenslund's program

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Table II. Vapor Pressures and Compositions of Mixtures at 25 °C

Dimethyl Sulfide (1) + Chloroform (2)

$n(C_2H_6S)$/mol	$n(CHCl_3)$/mol	p/Pa	x_2	y_2	$(p_{exptl} - p_{calcd})$/Pa
0.041 774 2	0.0	64 320			
0.041 774 2	0.005 196 1	57 900	0.1168	0.0286	−3
0.041 774 2	0.012 473 8	50 830	0.2385	0.0756	5
0.041 774 2	0.020 848 9	44 876	0.3411	0.1366	9
0.041 774 2	0.031 735 3	39 657	0.4085	0.1909	−61
0.057 799 3	0.039 008 4	41 090	0.4383	0.2191	60
0.031 945 5	0.039 008 4	34 156	0.5556	0.3568	−21
0.022 192 4	0.039 008 4	31 080	0.6424	0.4835	19
0.013 084 7	0.039 008 4	28 304	0.7520	0.6599	−10
0.004 929 7	0.039 008 4	26 602	0.8887	0.8679	3
0.0	0.039 008 4	26 254			

Diethyl Sulfide (1) + Chloroform (2)

$n(C_4H_{10}S)$/mol	$n(CHCl_3)$/mol	p/Pa	x_2	y_2	$(p_{exptl} - p_{calcd})$/Pa
0.034 184	0.0	7 852			
0.034 184	0.004 212	8 355	0.1090	0.1704	5
0.034 184	0.012 002	9 601	0.2580	0.4223	1
0.034 184	0.020 468	11 041	0.3720	0.5985	−15
0.034 184	0.033 304	13 143	0.4907	0.7492	7
0.034 184	0.049 494	15 331	0.5773	0.8339	16
0.028 256	0.039 101	15 065	0.5889	0.8436	3
0.018 888	0.039 101	17 420	0.6704	0.9009	−13
0.011 384	0.039 101	20 220	0.7711	0.9491	−22
0.004 339	0.039 101	23 764	0.8974	0.9841	42
0.0	0.039 101	26 254			

Dimethyl Sulfide (1) + Carbon Tetrachloride (2)

$n(C_2H_6S)$/mol	$n(CCl_4)$/mol	p/Pa	x_2	y_2	$(p_{exptl} - p_{calcd})$/Pa
0.040 525 3	0.0	64 352			
0.040 525 3	0.005 015 5	58 122	0.1165	0.0274	−11
0.040 525 3	0.009 708 6	53 514	0.2022	0.0532	1
0.040 525 3	0.016 445 5	48 345	0.2986	0.0982	6
0.040 525 3	0.023 379 5	44 296	0.3755	0.1244	−3
0.040 525 3	0.033 406 6	39 875	0.4605	0.1718	0
0.026 512 1	0.033 794 7	34 364	0.5705	0.2502	−3
0.008 816 4	0.033 794 7	23 606	0.8019	0,5283	16
0.005 850 6	0.033 794 7	21 055	0.8597	0.6224	−14
0.002 021 4	0.033 794 7	17 393	0.9468	0.9293	−5
0.0	0.033 794 7	15 220			

Diethyl Sulfide (1) + Carbon Tetrachloride (2)

$n(C_4H_{10}S)$/mol	$n(CCl_4)$/mol	p/Pa	x_2	y_2	$(p_{exptl} - p_{calcd})$/Pa
0.038 240 1	0.0	7 852			
0.038 240 1	0.004 106 7	8 299	0.0964	0.1459	7
0.038 240 1	0.009 726 8	8 843	0.2018	0.2981	−11
0.038 240 1	0.015 720 7	9 381	0.2901	0.4169	−8
0.038 240 1	0.024 834 4	10 081	0.3924	0.5422	2
0.038 240 1	0.030 000 0	10 880	0.4973	0.6556	23
0.032 546 5	0.035 511 6	11 020	0.5204	0.6785	−16
0.022 870 0	0.035 511 6	11 732	0.6066	0.7573	−1
0.014 468 9	0.035 511 6	12 601	0.7087	0.8376	8
0.008 228 1	0.035 511 6	13 494	0.8102	0.9046	−6
0.003 233 2	0.035 511 6	14 454	0.9156	0.9620	3
0.0	0.035 511 6	15 216			

Table III. Parameters in Eq 1 Fitted to the Data of Table II

mixture	g_0	g_1	g_2	g_3	σ/Pa	N
$C_2SH_6 + CCl_4$	−0.1594	0.0268			10	9
$C_4SH_{10} + CCl_4$	−0.2305				11	10
$C_2SH_6 + CHCl_3$	−0.8560	−0.0666	0.0438		37	9
$C_4SH_{10} + CHCL_3$	−0.9234	−0.0928	0.0296	0.0767	24	9

to determine the best fit UNIFAC parameters for the thioether systems. In this analysis we used the same division of the molecules into groups (CH_3, CH_3S, CH_2S, CH_2) as has been used by Fredenslund. As for the ethers, CH_3S and CH_2S groups have been assumed to be identical from the energetic point of view. The data on the thioether mixtures with CCl_4 were first used to determine the RS/CCl_4 and RS/R' parameters. These were then used with the data for the chloroform mixtures to determine the $RS/CHCl_3$ parameters as shown in Table IV.

Table IV. UNIFAC Parameters for Alkyl Sulfide Groups

Group Interaction Parameters

	CH_3	CH_2	CH_3S	CH_2S	CCl_4
CH_3	0.0	0.0	183.7[a]	183.7[a]	104.3
CH_2	0.0	0.0	183.7[a]	183.7[a]	104.3
CH_3S	−3.159[a]	−3.159[a]	0.0	0.0	9.994[a]
CH_2S	−3.159[a]	−3.159[a]	0.0	0.0	9.994[a]
CCl_4	−78.45	−78.45	19.65[a]	19.65[a]	0.0

	CH_3	CH_2	CH_3S	CH_2S	$CHCl_3$
CH_3	0.0	0.0	183.7[b]	183.7[b]	24.90
CH_2	0.0	0.0	183.7[b]	183.7[b]	24.90
CH_3S	−3.159[b]	−3.159[b]	0.0	0.0	−156.7[c]
CH_2S	−3.159[b]	−3.159[b]	0.0	0.0	−156.7[c]
$CHCl_3$	36.70	36.70	−13.87[c]	−13.87[c]	0.0

[a] Parameters evaluated from our experimental data on $CCl_4 + R_2S$. [b] Parameters from CCl_4 mixtures. [c] Parameters evaluated from our experimental data on $CHCl_3 + R_2S$.

Table V. Comparison of "Measured" Activity Coefficients with Those Recovered from UNIFAC Parameters

	halocarbon	alkyl sulfide		halocarbon	
	x_2	γ_1	$\gamma_1 - \gamma_1^{\mathrm{calcd}}$	γ_2	$\gamma_2 - \gamma_2^{\mathrm{calcd}}$
$(CH_3)_2S + CCl_4$	0.1165	0.997	0.0	0.872	0.001
	0.2022	0.991	0.001	0.901	0.0
	0.2986	0.982	0.002	0.928	-0.001
	0.3755	0.972	0.001	0.945	-0.002
	0.4605	0.961	0.001	0.961	-0.001
	0.5705	0.943	0.0	0.977	-0.001
	0.8019	0.906	0.0	0.997	0.001
	0.8597	0.896	-0.002	0.998	-0.001
	0.9468	0.883	0.0	0.999	0.0
$(C_2H_5)_2S + CCl_4$	0.0964	0.999	0.001	0.829	0.006
	0.2018	0.989	0.0	0.862	0.0
	0.2901	0.980	0.001	0.890	-0.002
	0.3924	0.965	0.003	0.919	-0.002
	0.4973	0.947	0.005	0.946	0.0
	0.5204	0.938	0.001	0.947	-0.004
	0.6066	0.919	0.002	0.965	-0.002
	0.7087	0.891	0.002	0.981	-0.001
	0.8102	0.859	-0.002	0.991	-0.001
	0.9156	0.824	-0.005	0.999	0.0
$(CH_3)_2S + CHCl_3$	0.1168	0.993	0.008	0.532	0.103
	0.2385	0.964	0.025	0.607	0.073
	0.3411	0.921	0.041	0.678	0.054
	0.4085	0.882	0.048	0.726	0.042
	0.4385	0.866	0.054	0.750	0.040
	0.5560	0.778	0.062	0.832	0.026
	0.6424	0.707	0.067	0.889	0.019
	0.7520	0.612	0.070	0.945	0.011
	0.8887	0.498	0.075	0.989	0.003
$(C_2H_5)_2S + CHCl_3$	0.1090	0.990	-0.003	0.502	-0.096
	0.2580	0.950	-0.013	0.603	-0.084
	0.3720	0.896	-0.026	0.682	-0.074
	0.4907	0.820	-0.043	0.769	-0.055
	0.5773	0.749	-0.061	0.833	-0.037
	0.5889	0.738	-0.065	0.841	-0.036
	0.6704	0.661	-0.083	0.896	-0.020
	0.7711	0.566	-0.099	0.951	-0.006
	0.8974	0.462	-0.095	0.994	0.003

Table VI. Comparison of UNIFAC and Barker Fits

	G^E(at $x = 0.5$, $T = 298$ K)/ J mol^{-1}		
mixture	exptl	Barker zeroth	UNIFAC
$n\text{-}C_6H_{14} + n\text{-}C_{16}H_{34}$	-69	-68[a]	-238
$CHCl_3 + CCl_4$	107	106[a]	97[b]
$n\text{-}C_6H_{14} + CCl_4$	144	143[a]	58[b]
$n\text{-}C_6H_{14} + CHCl_3$	342	343[a]	308[b]
$n\text{-}C_7H_{16} + CCl_4$	122	118[a]	34[b]
$n\text{-}C_7H_{16} + CHCl_3$	312	315[a]	281
$n\text{-}(C_3H_7)_2O + CCl_4$	-57	-54[a]	-55[b]
$n\text{-}(C_3H_7)_2O + CHCl_3$	-537	-529[a]	-424[b]
$n\text{-}C_8H_{18} + CCl_4$	95	100	4
$(CH_3)_3CCl + CCl_4$	268	373	16
$(ClC_2H_4)_2O + n\text{-}C_6H_{14}$	1317	238	546

[a] Data used in determination of Barker parameters. [b] Data used in determination of UNIFAC parameters.

The quality of the fit is shown in Table V where the input and recovered activity coefficients are compared.

As can be seen, the results for the carbon tetrachloride system are reproduced quite well and those for the chloroform mixtures are recovered less well. This may result from the accumulation of errors in the successive fitting of parameters or it may merely be a reflection of the very much larger deviation from ideality in the chloroform mixtures.

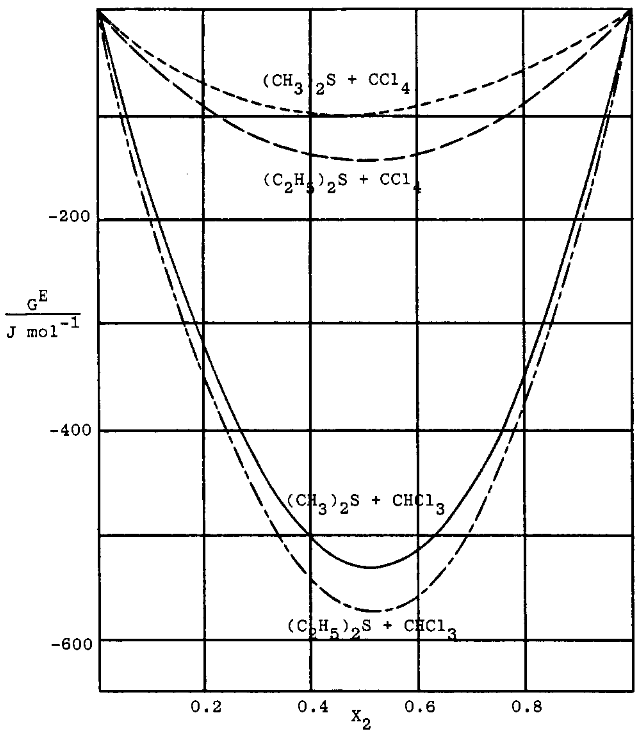

Figure 1. Excess Gibbs energies of mixtures of alkyl sulfides + halocarbons.

For comparison we show in Table VI the correlations achieved using the zeroth approximation of Barker's treatment and UNIFAC for a range of systems. The significant comparisons are those for systems data for which were not used in establishing the parameters for the correlation. As can be seen, the zeroth approximation to Barker's treatment and the UNIFAC are not very different in most of their predictions.

Registry No. CCl_4, 56-23-5; $CHCl_3$, 67-66-3; $(OH_3)_2S$, 75-18-3; $(C_2H_5)_2S$, 352-93-2.

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