Isothermal Vapor–Liquid Equilibrium of 1,2-Dibromoethane + Tetrachloromethane at Temperatures between 283.15 and 323.15 K

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Vapor pressures of 1,2-dibromoethane + tetrachloromethane, at 5 K intervals between 283.15 and 323.15 K, were measured by a static method. Activity coefficients and excess molar Gibbs free energies G^E were calculated by Barker's method. Reduction of the vapor pressure results is well represented by the Redlich–Kister, Wilson, and NRTL correlations.

Introduction

In previous papers, excess enthalpies (*1*) and dielectric behavior (*2*) of 1,2-dibromoethane + tetrachloromethane were measured. In this paper we report vapor pressures at nine temperatures between 283.15 and 323.15 K. As far as we know, the only previous measurements on this mixture are those of Birdi et al (*3*) at 293.15 K where G^E-(x=0.5) = 454 J mol^{-1} is about 10% higher than our value. These results can be used to understand conformational equilibrium in 1,2-dibromoethane and the proximity effect, and to determine the parameters in group contribution models.

Experimental Section

Tetrachloromethane was from Fluka (better than 99.8 mol % pure), and 1,2-dibromoethane was from Merck (better than 99 mol % pure). The liquids were used without further purification. Gas chromatography failed to show any significant impurities in 1,2-dibromoethane.

The total vapor pressure measurements were performed by a static method whose experimental details are described elsewhere (*4*, *5*). For preventing condensation effects on the mercury meniscus, the temperature of the manometer was maintained at 325.0 K by circulating water thermostated to ±0.1 K. The temperature of the liquid sample was measured by a set of Beckmann thermometers, previously checked against the vapor pressure of benzene (Merck, better than 99.9 mol %), along with Ambrose's equation (*6*) relating temperature (T_{68}) with pressure by means of a sum of Chebyshev polynomials up to degree 6. The liquids were degassed by magnetic stirring under their own vapor pressures before mixing. The cell containing

Table 1. Vapor Pressure P and Molar Volumes V of the Pure Compounds Used in the Barker Analysis

	tetrachloromethane			1,2-dibromoethane		
		P°/kPa			P°/kPa	
T/K	V°/(cm^3·mol^{-1})[a]	this work	lit. (*7*)	V°/(cm^3·mol^{-1})[a]	this work	lit.
283.15	95.08	7.507	7.514	85.17	0.595	0.580 (*8*)
288.15	95.75	9.600	9.603	85.65	0.840	
293.15	96.43	12.127	12.149	86.13	1.120	1.072 (*3*, *8*)
298.15	97.11	15.211	15.227	86.62	1.515	1.612 (*9*)
303.15	97.81	18.928	18.915	87.11	1.993	1.932 (*8*)
308.15	98.52	23.291	23.300	87.62	2.606	2.949 (*10*)
313.15	99.24	28.468	28.478	88.13	3.369	
318.15	99.97	34.530	34.546	88.64	4.336	
323.15	100.71	41.517	41.615	89.15	5.477	

[a] Experimental.

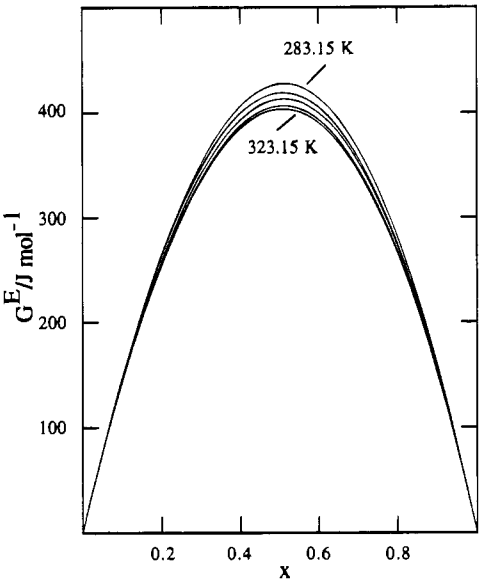

Figure 1. Excess molar Gibbs energies G^E, at 10 K intervals, for x 1,2-$C_2H_4Br_2$ + (1 − x) CCl_4.

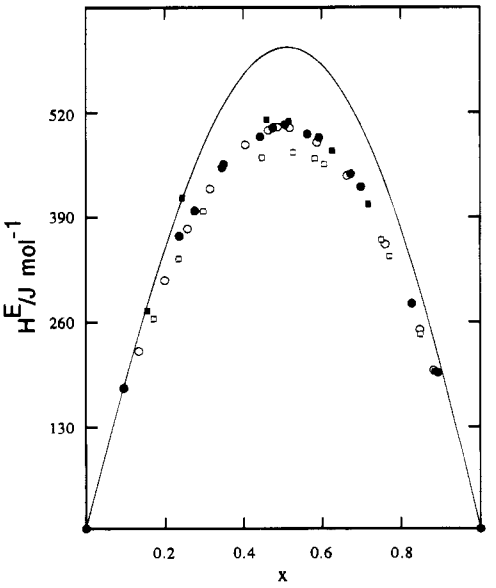

Figure 2. Excess molar enthalpies, H^E, at 298.15 K, for x 1,2-$C_2H_4Br_2$ + (1 − x) CCl_4: solid line, this work from the Gibbs–Helmholtz equation; (○) ref 1; (●) ref 17; (□) ref 18; (■) ref 19.

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Table 2. Experimental Vapor Pressure Data, Activity Coefficients, and Excess Molar Gibbs Energy Calculated from Redlich–Kister, Wilson, and NRTL Correlations for CCl_4 (1) + 1,2-$C_2H_4Br_2$ (2)

		Redlich–Kister			Wilson			NRTL		
x_2	P/kPa	γ_1	γ_2	G^E/(J·mol^{-1})	γ_1	γ_2	G^E/(J·mol^{-1})	γ_1	γ_2	G^E/(J·mol^{-1})
					283.15 K					
0.0725	7.053	1.0033	1.8271	110	1.0035	1.8330	111	1.0034	1.8290	110
0.2111	6.291	1.0293	1.5660	277	1.0301	1.5646	278	1.0296	1.5655	277
0.2745	5.965	1.0508	1.4684	333	1.0517	1.4666	334	1.0511	1.4678	333
0.3892	5.370	1.1075	1.3212	402	1.1081	1.3204	402	1.1077	1.3210	402
0.4634	5.004	1.1583	1.2438	424	1.1583	1.2440	424	1.1583	1.2438	424
0.6297	4.110	1.3244	1.1133	404	1.3222	1.1151	405	1.3237	1.1138	404
0.7523	3.249	1.5087	1.0504	327	1.5063	1.0521	329	1.5080	1.0509	327
0.8222	2.700	1.6458	1.0260	258	1.6458	1.0272	260	1.6458	1.0263	259
0.9245	1.632	1.9022	1.0047	125	1.9141	1.0051	126	1.9056	1.0048	125
					288.15 K					
0.0725	9.071	1.0031	1.7980	109	1.0035	1.8093	111	1.0034	1.8058	110
0.2112	8.043	1.0282	1.5498	274	1.0298	1.5466	276	1.0294	1.5475	276
0.2747	7.631	1.0493	1.4548	330	1.0512	1.4509	332	1.0506	1.4520	331
0.3895	6.894	1.1055	1.3103	399	1.1066	1.3086	399	1.1062	1.3091	399
0.4636	6.446	1.1558	1.2342	420	1.1556	1.2346	420	1.1556	1.2345	420
0.6300	5.256	1.3188	1.1066	398	1.3143	1.1100	400	1.3158	1.1089	399
0.7525	4.194	1.4946	1.0464	320	1.4902	1.0496	324	1.4918	1.0485	323
0.8224	3.474	1.6218	1.0236	252	1.6223	1.0258	256	1.6223	1.0251	255
0.9246	2.114	1.8511	1.0042	120	1.8728	1.0048	124	1.8656	1.0046	123
					293.15 K					
0.0726	11.424	1.0035	1.7875	111	1.0034	1.7863	110	1.0034	1.7833	110
0.2113	10.211	1.0298	1.5288	275	1.0296	1.5294	275	1.0291	1.5301	274
0.2749	9.643	1.0509	1.4352	330	1.0507	1.4358	330	1.0502	1.4368	329
0.3896	8.747	1.1051	1.2973	396	1.1050	1.2976	396	1.1047	1.2979	396
0.4639	8.135	1.1529	1.2256	416	1.1530	1.2256	416	1.1531	1.2254	416
0.6303	6.625	1.3063	1.1054	395	1.3067	1.1052	395	1.3080	1.1041	394
0.7528	5.266	1.4748	1.0473	319	1.4750	1.0471	319	1.4762	1.0462	317
0.8226	4.390	1.6000	1.0246	252	1.5999	1.0245	252	1.5997	1.0238	250
0.9248	2.710	1.8355	1.0045	121	1.8344	1.0045	121	1.8278	1.0043	120
					298.15 K					
0.0726	14.361	1.0033	1.7589	109	1.0033	1.7600	109	1.0032	1.7571	109
0.2115	12.808	1.0285	1.5144	272	1.0286	1.5143	273	1.0282	1.5150	272
0.2753	12.143	1.0490	1.4243	327	1.0492	1.4241	327	1.0487	1.4250	327
0.3900	10.947	1.1019	1.2906	393	1.1020	1.2905	393	1.1017	1.2909	393
0.4639	10.230	1.1484	1.2209	413	1.1484	1.2210	413	1.1485	1.2209	413
0.6308	8.337	1.2992	1.1027	392	1.2988	1.1031	393	1.3000	1.1022	392
0.7531	6.642	1.4634	1.0459	317	1.4628	1.0464	317	1.4641	1.0455	316
0.8228	5.550	1.5847	1.0238	250	1.5846	1.0241	251	1.5846	1.0235	249
0.9249	3.462	1.8106	1.0043	120	1.8134	1.0044	121	1.8075	1.0043	120
					303.15 K					
0.0727	17.861	1.0033	1.7350	109	1.0032	1.7323	108	1.0031	1.7297	108
0.2118	15.949	1.0282	1.4965	270	1.0277	1.4977	270	1.0274	1.4984	269
0.2759	15.117	1.0482	1.4096	325	1.0477	1.4109	324	1.0473	1.4117	324
0.3904	13.640	1.0992	1.2819	390	1.0989	1.2825	390	1.0987	1.2828	390
0.4643	12.734	1.1439	1.2153	410	1.1440	1.2152	410	1.1441	1.2151	410
0.6315	10.342	1.2893	1.1014	390	1.2904	1.1005	389	1.2916	1.0997	389
0.7536	8.275	1.4487	1.0459	315	1.4497	1.0453	315	1.4508	1.0444	314
0.8231	6.929	1.5678	1.0240	250	1.5675	1.0236	249	1.5675	1.0230	247
0.9251	4.376	1.7937	1.0044	121	1.7892	1.0043	120	1.7836	1.0042	119
					308.15 K					
0.0729	21.980	1.0034	1.7162	109	1.0032	1.7123	108	1.0031	1.7101	108
0.2122	19.666	1.0282	1.4809	270	1.0275	1.4825	269	1.0272	1.4831	268
0.2766	18.636	1.0481	1.3956	323	1.0474	1.3974	323	1.0470	1.3982	323
0.3910	16.815	1.0980	1.2718	387	1.0977	1.2725	387	1.0975	1.2728	387
0.4648	15.688	1.1416	1.2075	406	1.1418	1.2073	406	1.1419	1.2072	406
0.6322	12.756	1.2824	1.0975	385	1.2841	1.0963	384	1.2851	1.0955	384
0.7542	10.200	1.4355	1.0442	311	1.4369	1.0431	310	1.4379	1.0424	309
0.8236	8.547	1.5494	1.0231	246	1.5490	1.0224	244	1.5490	1.0219	243
0.9253	5.470	1.7643	1.0043	119	1.7573	1.0041	118	1.7524	1.0040	117
					313.15 K					
0.0730	26.883	1.0032	1.6916	108	1.0031	1.6899	107	1.0030	1.6878	107
0.2127	24.049	1.0272	1.4679	267	1.0269	1.4688	267	1.0265	1.4694	267
0.2776	22.785	1.0467	1.3852	321	1.0464	1.3861	321	1.0460	1.3869	321
0.3918	20.561	1.0955	1.2652	384	1.0954	1.2656	384	1.0952	1.2659	384
0.4653	19.200	1.1381	1.2026	403	1.1382	1.2025	404	1.1383	1.2024	404
0.6323	15.605	1.2759	1.0950	383	1.2767	1.0944	382	1.2777	1.0937	382
0.7542	12.567	1.4250	1.0428	309	1.4255	1.0424	308	1.4265	1.0417	308
0.8240	10.496	1.5357	1.0222	244	1.5354	1.0219	243	1.5354	1.0214	242
0.9256	6.777	1.7412	1.0041	117	1.7382	1.0040	117	1.7337	1.0039	116
					318.15 K					
0.0733	32.609	1.0031	1.6682	107	1.0030	1.6667	106	1.0029	1.6647	106
0.2133	29.206	1.0263	1.4551	266	1.0260	1.4559	265	1.0257	1.4564	265

Table 2 (Continued)

		Redlich–Kister			Wilson			NRTL		
x_2	P/kPa	γ_1	γ_2	G^E/(J·mol^{-1})	γ_1	γ_2	G^E/(J·mol^{-1})	γ_1	γ_2	G^E/(J·mol^{-1})
					318.15 K					
0.2788	27.651	1.0454	1.3750	320	1.0451	1.3758	319	1.0447	1.3766	319
0.3928	24.958	1.0929	1.2595	382	1.0928	1.2598	382	1.0925	1.2601	382
0.4660	23.279	1.1343	1.1988	401	1.1344	1.1988	402	1.1344	1.1987	402
0.6332	19.020	1.2694	1.0935	381	1.2701	1.0930	381	1.2710	1.0923	381
0.7548	15.281	1.4156	1.0423	308	1.4161	1.0419	308	1.4171	1.0413	307
0.8239	12.874	1.5234	1.0221	244	1.5232	1.0219	243	1.5233	1.0214	242
0.9259	8.397	1.7267	1.0040	117	1.7243	1.0040	116	1.7200	1.0038	116
					323.15 K					
0.0735	39.306	1.0033	1.6631	108	1.0031	1.6587	107	1.0030	1.6567	107
0.2141	35.202	1.0272	1.4442	268	1.0265	1.4461	267	1.0261	1.4467	267
0.2803	33.311	1.0468	1.3637	322	1.0459	1.3658	321	1.0456	1.3665	321
0.3940	30.059	1.0938	1.2507	383	1.0935	1.2515	383	1.0932	1.2519	383
0.4670	28.063	1.1343	1.1921	401	1.1346	1.1918	401	1.1346	1.1918	401
0.6344	22.909	1.2657	1.0904	379	1.2679	1.0888	378	1.2687	1.0882	378
0.7556	18.453	1.4066	1.0411	306	1.4085	1.0398	304	1.4093	1.0392	303
0.8245	15.563	1.5108	1.0216	242	1.5104	1.0206	240	1.5105	1.0202	239
0.9264	10.222	1.7088	1.0039	116	1.6996	1.0037	114	1.6962	1.0036	113

Table 3. Parameters and Standard Deviations $\sigma(P)$ of Eqs 1–3 for CCl_4 (1) + 1,2-$C_2H_4Br_2$ (2)

	Redlich–Kister				Wilson			NRTL		
T/K	A_0	A_1	A_2	$\sigma(P)$/Pa	$(\lambda_{12}-\lambda_{11})$/(J·mol^{-1})	$(\lambda_{21}-\lambda_{22})$/(J·mol^{-1})	$\sigma(P)$/Pa	$(g_{12}-g_{22})$/(J·mol^{-1})	$(g_{21}-g_{11})$/(J·mol^{-1})	$\sigma(P)$/Pa
283.15	0.7264	−0.0367	0.0006	11	983	935	11	1334	506	11
288.15	0.7067	−0.0271	−0.0113	15	919	708	17	1255	556	16
293.15	0.6878	−0.0249	0.0106	17	850	1010	16	1172	611	16
298.15	0.6725	−0.0266	0.0060	18	865	984	17	1215	561	18
303.15	0.6555	−0.0299	0.0134	19	869	960	19	1242	518	20
308.15	0.6388	−0.0248	0.0149	19	806	996	20	1169	566	23
313.15	0.6247	−0.0253	0.0104	21	811	978	21	1197	528	23
318.15	0.6119	−0.0293	0.0098	24	845	936	23	1269	452	25
323.15	0.6009	−0.0225	0.0159	43	753	1013	45	1151	555	48

the sample was immersed in a water bath, the temperature of which was maintained constant within better than ±5 mK using a Haake F3 instrument. Manometer readings were made with a Wild KM-305 cathetometer to within ±0.01 mm. The reproducibility of the pressure measurements is estimated to be better than ±10 Pa. Errors in the mole fraction are estimated to be less than ±0.0002. A densimeter (Anton Paar DMA 60/DMA 602) was used for the density measurements on the pure components.

Results

Molar volumes and vapor pressures of the pure compounds are collected in Table 1. The virial coefficient of tetrachloromethane (B_{11} = −1330 cm^3 mol^{-1}) at 325.0 K was obtained from those values tabulated by Dymond and Smith (*11*), and that of 1,2-dibromoethane (B_{22} = −3442 cm^3 mol^{-1}) from the Tsonopoulos correlation (*12*). The cross virial coefficient (B_{12} = −2221 cm^3 mol^{-1}) was calculated using a Lorentz-type combination rule.

Table 2 shows our vapor pressure measurements along with the activity coefficients γ_1 and γ_2 and the excess molar Gibbs free energy G^E values fitted to the Redlich–Kister, Wilson (*13*), and NRTL (*14*) correlations by Barker's method (*15*).

Redlich–Kister:

$$G^E/RT = x_1x_2\sum_{i=0}^{2}A_i(x_1-x_2)^i \qquad (1)$$

Wilson:

$$G^E/RT = -x_1\ln(x_1+\Lambda_{12}x_2) - x_2\ln(x_2+\Lambda_{21}x_1) \qquad (2)$$

where

$$\Lambda_{ij} = \frac{V_j^\circ}{V_i^\circ}\exp\left(-\frac{\lambda_{ij}-\lambda_{ii}}{RT}\right)$$

NRTL:

$$\frac{G^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1+x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2+x_1G_{12}}\right) \qquad (3)$$

with

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad \text{and} \quad \tau_{ij} = \frac{g_{ij}-g_{jj}}{RT}$$

V° is the molar volume, x_2 is the mole fraction of 1,2-dibromoethane, and λ's and g's are energy parameters of interaction between the molecules designated in the subscripts. The parameter α_{12} is related to the nonrandomness in the mixture and for which we have used the typical value α_{12} = 0.3 (*16*). For a given composition, the sample temperature is changed and a slight variation of the true liquid mole fraction may be detected in Table 2 according to the variable composition of the vapor phase. The coefficients of eqs 1–3 together with the standard deviations are collected in Table 3. The vapor pressure data are well represented by the three correlations. Excess molar Gibbs energy curves, at 10 K intervals, are shown in Figure 1, and a negative temperature coefficient is observed.

By regarding the molar excess enthalpy H^E as independent of the temperature, we have fitted G^E/T data with a first-degree polynomial in $1/T$, and according to the Gibbs–Helmholtz equation the derivative gives H^E. The H^E-calculated values at round mole fractions are shown as a curve in Figure 2 together with experimental data found in the literature. At x = 0.5, the calculated excess

enthalpy is about 20% higher than the experimental value.

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