266 J. Chem. Eng. Data 1990, 35, 266-271

Isothermal Vapor–Liquid Equilibria, Excess Enthalpies, and Excess Volumes of 1-Chlorobutane + Tetrachloromethane, 1,2-Dichloroethane + Tetrachloromethane, and 1,2-Dichloroethane + 1-Chlorobutane Mixtures[†]

José Muñoz Embid[‡] and Charles Berro

Laboratoire de Chimie-Physique, Faculté des Sciences de Luminy, 13288 Marseille Cedex 9, France

Santos Otín

Departamento de Química Orgánica—Química Física, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain

Henry V. Kehiaian*

Institut de Topologie et de Dynamique des Systèmes, Université de Paris VII-CNRS, 1, Rue Guy de la Brosse,
75005 Paris, France

Isothermal vapor–liquid equilibria (VLE); molar excess enthalpies H^E, at 313.15 K; and molar excess volumes V^E, at 298.15 K, have been measured for liquid 1-chlorobutane + tetrachloromethane, 1,2-dichloroethane + tetrachloromethane, and 1,2-dichloroethane + 1-chlorobutane mixtures. The VLE data were reduced by applying the maximum likelihood principle. The molar excess Gibbs energy, G^E, derived from the VLE data, and the H^E compare satisfactorily with group contribution (DISQUAC) predictions.

Introduction

Chloroalkanes represent a class of technically important compounds, used in industry as intermediates or as final products. In view of the variety of possible mixtures, a large number of systems should be investigated experimentally in order to have the data needed in designing distillation columns and other stills for chemical plants. Therefore, the applicability of predictive methods is of great interest. However, the occurrence of strong intramolecular effects, especially of the proximity effect, renders the widely used empirical methods, ASOG and UNIFAC, quite inaccurate (*3*).

DISQUAC is a group contribution method, derived from the lattice model, which improves the quality of the predictions by using structure-dependent group parameters. It has been applied to several classes of systems, including also mixtures containing chloroalkanes (*4*, *5*).

In this work, we have measured the vapor–liquid equilibria (VLE) and the molar excess enthalpies H^E at 313.15 K of tetrachloromethane + 1-chlorobutane or + 1,2-dichloroethane. The purpose was to check the previously published (*4*) DISQUAC predictions for these two mixtures.

Moreover, we have measured the VLE and H^E of 1,2-dichloroethane + 1-chlorobutane at 313.15 K, a system never investigated before. The purpose was to calculate the DISQUAC parameters of 1,2-dichloroethane + 1-chlorobutane and to estimate therefrom the parameters of other α,ω-dichloroalkane + 1-chloroalkane mixtures. Indeed, the Cl/alkane or Cl/CCl_4 interaction parameters of the Cl groups (Cl″) in α,ω-dichloroalkanes, $ClCH_2(CH_2)_{n-2}CH_2Cl$, vary with the number n of C atoms and reach the values of the Cl group (Cl′) in 1-chloroalkanes, $CH_3(CH_2)_{n-2}CH_2Cl$, for $n \geq 5$ (*4*, *5*), i.e., when the distance between the two Cl atoms is sufficiently large (disappearance of the proximity effect). We expect to obtain a similar regular change of the Cl′/Cl″ parameters from a determinable value, for $n = 2$ ($ClCH_2CH_2Cl$), to a vanishing value, for $n \geq 5$.

Table I. Densities ρ_i° and Vapor Pressure P_i° of the Pure Components

	ρ_i°(298.15 K)/(g cm^{-3}) this work	ρ_i°(298.15 K)/(g cm^{-3}) lit. (*21*)	P_i°(313.15 K)/(10^3 Pa) this work	P_i°(313.15 K)/(10^3 Pa) lit. (*21*)
1-chlorobutane	0.880 88	0.880 4	25.873	25.884
1,2-dichloroethane	1.245 58	1.245 61	20.740	20.723
tetrachloromethane	1.584 25	1.584 62	28.439	28.440

Experimental Section

Materials. All the chemicals were from Merck. Tetrachloromethane and 1-chlorobutane were "pro analysi" products, with stated minimum purities 99.8 and 99.7 mol %, respectively: 1,2-dichloroethane was 99.7 mol % "Uvasol" grade reagent.

In Table I, we compare the measured densities and vapor pressures of the products with literature values.

Apparatus and Procedure. Vapor–liquid equilibrium data were determined at constant temperature in a still designed by Berro et al. (*6*).

The temperature inside the equilibrium cell was measured by means of a Lauda Model R42 digital thermometer with a platinum sensor, which has a precision of 0.01 K. The pressure was measured by means of a Digiquartz pressure transducer of Paroscientific Inc., Model 215A, calibrated in the pressure range 0–10 MPa. The estimated precision of the pressure measurements is $\sigma_e(P) = 2$ Pa.

Liquid and vapor mole fractions, x_i and y_i, respectively, were determined by densimetric analysis using an Anton Paar Model DMA 60 densimeter equipped with two DMA 601M cells in a flow system as described previously (*6*). The cells were thermoregulated to better than 0.1 K, and the temperature was measured with the same Lauda Model R42 digital thermometer with another platinum sensor.

The densities were previously determined to better than $\sigma_e(\rho^\circ) = 0.00002$ g cm^{-3} in the same densimeter. Binary

---

[†] This paper is a contribution to the TOM Project (*1*): Thermodynamics of binary mixtures containing chloroalkanes. V. Part IV: Reference 2.

[‡] On leave of absence from the Departamento de Química Orgánica-Química Física, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain.

0021-9568/90/1735-0266$02.50/0

Table II. Excess Molar Volumes V^E at 298.15 K as a Function of Mole Fraction x_1, Coefficients A_j, Equation 1, and Standard Deviations $\sigma_m(V^E)$, Equation 2

1-Chlorobutane (1) + Tetrachloromethane (2)

x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})
0.0578	−0.017	0.3815	−0.121	0.6723	−0.132
0.0798	−0.027	0.4314	−0.126	0.7061	−0.133
0.1101	−0.035	0.4542	−0.129	0.7468	−0.127
0.1407	−0.048	0.5013	−0.135	0.7832	−0.113
0.1993	−0.068	0.5338	−0.138	0.8264	−0.100
0.2192	−0.071	0.5638	−0.140	0.8919	−0.074
0.2626	−0.089	0.5844	−0.142	0.9288	−0.059
0.2971	−0.097	0.6258	−0.140	0.9563	−0.041
0.3583	−0.114				

$$V^E/x_1(1-x_1)\ \text{cm}^3\ \text{mol}^{-1} = -0.5422 - 0.170(2x_1-1) - 0.053(2x_1-1)^2 - 0.165(2x_1-1)^3$$

$$\sigma_m(V^E)/(\text{cm}^3\ \text{mol}^{-1}) = 0.0025$$

1,2-Dichloroethane (1) + Tetrachloromethane (2)

x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})
0.0511	0.075	0.4276	0.297	0.7862	0.147
0.1162	0.152	0.4590	0.291	0.8080	0.132
0.1727	0.203	0.4979	0.291	0.8466	0.104
0.1985	0.225	0.5595	0.273	0.8673	0.086
0.2601	0.261	0.6217	0.246	0.9139	0.052
0.3085	0.273	0.6559	0.236	0.9376	0.035
0.3548	0.288	0.6823	0.219	0.9431	0.031
0.3872	0.293	0.7044	0.204	0.9617	0.020
0.3948	0.293	0.7653	0.162	0.9677	0.017

$$V^E/x_1(1-x_1)\ \text{cm}^3\ \text{mol}^{-1} = 1.1557 - 0.355(2x_1-1) - 0.080(2x_1-1)^2 - 0.254(2x_1-1)^3$$

$$\sigma_m(V^E)/(\text{cm}^3\ \text{mol}^{-1}) = 0.0020$$

1,2-Dichloroethane (1) + 1-Chlorobutane (2)

x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})
0.0406	0.024	0.3201	0.178	0.6492	0.185
0.0779	0.050	0.3789	0.191	0.7103	0.171
0.0815	0.053	0.4297	0.200	0.7317	0.160
0.1177	0.081	0.4526	0.196	0.7839	0.140
0.1675	0.110	0.4848	0.200	0.8345	0.114
0.1775	0.115	0.5155	0.200	0.8911	0.082
0.2523	0.154	0.5661	0.196	0.9343	0.053
0.2794	0.162	0.5989	0.196	0.9637	0.031

$$V^E/x_1(1-x_1)\ \text{cm}^3\ \text{mol}^{-1} = 0.8024 - 0.018(2x_1-1) + 0.118(2x_1-1)^2 + 0.133(2x_1-1)^3 - 0.213(2x-1)^4$$

$$\sigma_m(V^E)/(\text{cm}^3\ \text{mol}^{-1}) = 0.0018$$

Table III. Excess Molar Enthalpies H^E at 313.15 K as a Function of Mole Fraction x_1, Coefficients A_j, Equation 1, and Standard Deviations $\sigma_m(H^E)$, Equation 2

1-Chlorobutane (1) + Tetrachloromethane (2)

x_1	H^E/ (J mol^{-1})	x_1	H^E/ (J mol^{-1})	x_1	H^E/ (J mol^{-1})
0.1010	1	0.5230	0	0.8341	−4
0.1721	3	0.6543	−2	0.9161	−1
0.4310	1	0.7720	−1		

$$H^E/x_1(1-x_1)\ \text{J mol}^{-1} = 0.6 - 25.5(2x_1-1)$$

$$\sigma_m(H^E)/(\text{J mol}^{-1}) = 1.0$$

1,2-Dichloroethane (1) + Tetrachloromethane (2)

x_1	H^E/ (J mol^{-1})	x_1	H^E/ (J mol^{-1})	x_1	H^E/ (J mol^{-1})
0.0873	212	0.4015	637	0.7198	550
0.1361	304	0.4852	655	0.8050	431
0.2005	422	0.5311	664	0.8873	274
0.3173	575	0.6047	634		

$$H^E/x_1(1-x_1)\ \text{J mol}^{-1} = 2651.4 + 85(2x_1-1) + 83(2x_1-1)^2$$

$$\sigma_m(H^E)/(\text{J mol}^{-1}) = 4.7$$

1,2-Dichloroethane (1) + 1-Chlorobutane (2)

x_1	H^E/ (J mol^{-1})	x_1	H^E/ (J mol^{-1})	x_1	H^E/ (J mol^{-1})
0.0998	106	0.3120	311	0.6925	292
0.1365	145	0.4100	350	0.7793	233
0.1694	190	0.5287	347	0.8809	155
0.2410	260	0.5912	326		

$$H^E/x_1(1-x_1)\ \text{J mol}^{-1} = 1408.9 - 246(2x_1-1) - 90(2x_1-1)^2 + 712(2x_1-1)^3$$

$$\sigma_m(H^E)/(\text{J mol}^{-1}) = 3.7$$

mixtures were prepared by weighing, using the technique designed by Berro and Péneloux (*7*), to prevent the partial evaporation of the liquid. V^E was calculated from the densities.

Molar excess enthalpies were determined by using an isobaric and quasi-isothermic calorimeter similar to that described in ref 8. Electrical energy was measured to better than 0.5%. The temperature in the water bath was controlled to within 0.002 K. The estimated errors are $\sigma_e(x_i) < 0.0002$ and $\sigma_e(T) = 0.01$ K (*9*). The calorimeter was checked against hexane + cyclohexane, at 298.15 K, the agreement with the data of ref 10 being better than 0.5% over the central range of concentration.

Experimental Results and Treatment of Data

Molar Excess Enthalpies and Volumes. The V^E values at 298.15 K and H^E values at 313.15 K are collected in Tables II and III. A smoothing equation of the type

$$Q_{calc}/x_1(1-x_1) = \sum A_j(2x_1-1)^{j-1} \qquad (1)$$

where $Q = V^E$ or H^E, was fitted by the method of least squares. The A_j parameters are given in Tables II and III together with the standard deviations $\sigma_m(Q)$ calculated as

$$\sigma_m(Q) = \{\sum(Q - Q_{calc})^2/(N-m)\}^{1/2} \qquad (2)$$

where N is the number of experimental values Q and m is the number of parameters A_j.

Vapor–Liquid Equilibrium Data. The experimental vapor–liquid equilibrium data are listed in Table IV. Data reduction was performed with use of the "observed deviation" reduction method proposed by Neau and Péneloux (*11*). In this method, G^E is fitted to a Redlich–Kister polynomial of the form

$$G^E/x_1(1-x_1)RT = \sum(2j-1)A_j(2x_1-1)^{j-1} \qquad (3)$$

The A_j parameters are obtained by applying the maximum likelihood principle to the objective function S defined in Appendix A of ref 12. Vapor-phase nonideality and the liquid-phase Poynting correction were accounted for in terms of the molar second virial coefficients B_{ij}, estimated by the method of Hayden and O'Connell (*13*), and the liquid molar volumes V_i°. The thermodynamic consistency of the measured VLE data was checked by using the weighted root mean square deviation, WRMSD, defined as

$$\text{WRMSD} = [S/(2N-m)]^{1/2} \qquad (4)$$

The WRMSD found in this way should be equal to 1 for perfectly consistent data; a value close to 2 would indicate that there are systematic errors of the same magnitude as the random errors in measurements (*12*). Results of the reduction of our VLE data are given in Table IV.

Results

The experimental V^E and H^E values are shown in Figures 1 and 2, respectively, compared with the available literature values. The V^E of 1,2-dichloroethane + tetrachloromethane measured in this work at 298.15 K is ca. 10% lower than the value reported by Wilhelm et al. (*14*) at the same temperature. The discrepancies with the measurements of other authors may be due, in part, to differences in the experimental temperatures. No H^E or V^E data were found in the literature for 1,2-dichloroethane + 1-chlorobutane.

Table IV. Experimental Vapor–Liquid Equilibrium Pressure P and Vapor Mole Fraction y_1 at 313.15 K as a Function of Liquid Mole Fraction x_1, Coefficients A_j, Equation 3, Weighted Root Mean Square Deviation WRMSD, Equation 4, Standard Deviations $\sigma(P)$ and $\sigma(y_1)$, Equation 5, Molar Second Virial Coefficients B_{ij}, and Liquid Molar Volumes of Pure Components V_i°

x_1	y_1	$P/(10^3\ \mathrm{Pa})$	x_1	y_1	$P/(10^3\ \mathrm{Pa})$
1-Chlorobutane (1) + Tetrachloromethane (2)					
0.0716	0.0742	28.530	0.5669	0.5355	27.749
0.0850	0.0874	28.543	0.6095	0.5769	27.595
0.1438	0.1438	28.558	0.6283	0.5954	27.534
0.2004	0.1967	28.544	0.6429	0.6099	27.477
0.2299	0.2238	28.519	0.6452	0.6122	27.454
0.2741	0.2640	28.464	0.6777	0.6449	27.344
0.3144	0.3007	28.397	0.7225	0.6907	27.163
0.3520	0.3349	28.333	0.8052	0.7780	26.800
0.4091	0.3871	28.205	0.8578	0.8356	26.556
0.4712	0.4447	28.041	0.9116	0.8962	26.331
0.5232	0.4937	27.886	0.9593	0.9516	26.099
$G^E/x_1(1-x_1)RT = 0.11562 - 0.01302(2x_1 - 1)$					
$\sigma(P)/(10^3\ \mathrm{Pa}) = 0.012;\ \sigma(y_1) = 0.00047$					
WRMSD = 1.12					
$B_{11}/(\mathrm{cm^3\ mol^{-1}}) = -1650;\ B_{22}/(\mathrm{cm^3\ mol^{-1}}) = -1006;\ B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -1242$					
$V_1^\circ/(\mathrm{cm^3\ mol^{-1}}) = 105;\ V_2^\circ/(\mathrm{cm^3\ mol^{-1}}) = 98$					
1,2-Dichloroethane (1) + Tetrachloromethane (2)					
0.0612	0.0731	28.784	0.5496	0.4604	28.017
0.1331	0.1460	29.073	0.5928	0.4915	27.690
0.1482	0.1600	29.112	0.6436	0.5302	27.224
0.1995	0.2048	29.190	0.6904	0.5689	26.720
0.2241	0.2254	29.198	0.7240	0.5988	26.313
0.2505	0.2465	29.189	0.7935	0.6676	25.349
0.3001	0.2843	29.133	0.8357	0.7152	24.621
0.3415	0.3146	29.049	0.8529	0.7364	24.314
0.3925	0.3507	28.886	0.8886	0.7861	23.600
0.4499	0.3906	28.639	0.9085	0.8186	23.137
0.4968	0.4230	28.384	0.9505	0.8916	22.129
$G^E/x_1(1-x_1)RT = 0.57070 + 0.00857(2x_1 - 1) - 0.00168(2x_1 - 1)^2$					
$\sigma(P)/(10^3\ \mathrm{Pa}) = 0.010;\ \sigma(y_1) = 0.00089$					
WRMSD = 1.81					
$B_{11}/(\mathrm{cm^3\ mol^{-1}}) = -1291;\ B_{22}/(\mathrm{cm^3\ mol^{-1}}) = -1006;\ B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -1031$					
$V_1^\circ(\mathrm{cm^3/mol^{-1}}) = 80;\ V_2^\circ/(\mathrm{cm^3\ mol^{-1}}) = 98$					
1,2-Dichloroethane (1) + 1-Chlorobutane (2)					
0.0589	0.0580	25.783	0.5954	0.5336	24.314
0.1149	0.1113	25.742	0.6349	0.5693	24.064
0.1803	0.1717	25.671	0.6665	0.5988	23.912
0.2340	0.2197	25.591	0.7034	0.6344	23.731
0.2901	0.2690	25.467	0.7474	0.6770	23.356
0.3497	0.3207	25.313	0.7875	0.7195	23.034
0.4013	0.3651	25.153	0.8223	0.7573	22.708
0.4361	0.3951	25.028	0.8579	0.7995	22.357
0.4737	0.4273	24.875	0.8923	0.8427	22.107
0.5086	0.4574	24.726	0.9322	0.8955	21.670
0.5488	0.4923	24.530	0.9660	0.9437	21.220
$G^E/x_1(1-x_1)RT = 0.25093 + 0.01291(2x_1 - 1)$					
$\sigma(P)/(10^3\ \mathrm{Pa}) = 0.041;\ \sigma(y_1) = 0.00095$					
WRMSD = 1.42					
$B_{11}/(\mathrm{cm^3\ mol^{-1}}) = -1291;\ B_{22}/(\mathrm{cm^3\ mol^{-1}}) = -1650;\ B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -1458$					
$V_1^\circ/(\mathrm{cm^3\ mol^{-1}}) = 80;\ V_2^\circ/(\mathrm{cm^3\ mol^{-1}}) = 105$					

The experimental P–x–y data are shown in Figure 3. VLE measurements have been reported in the literature for 1,2-dichloroethane + tetrachloromethane only. To the isothermal data listed in Table I of ref 4, we must add the recent measurements of López et al. (*15*) at 298.15 K and several isobaric data (see ref 16–18).

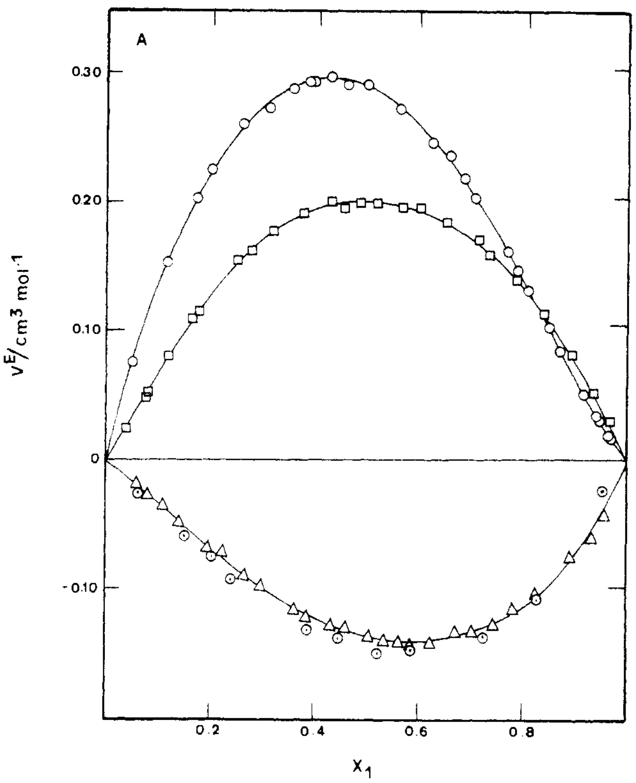

Figure 1. Excess molar volumes V^E as a function of mole fraction x_1. Curves, smoothed values, eq 1, at 298.15 K (this work); points, direct experimental values: (A) (○) 1,2-dichloroethane (1) + CCl_4 (2) at 298.15 K (this work), (□) 1,2-dichloroethane (1) + 1-chlorobutane (2) at 298.15 K (this work), (△) 1-chlorobutane (1) + CCl_4 (2) at 298.15 K (this work), (⊙) 1-chlorobutane (1) + CCl_4 (2) at 293.15 K (*25*); (B) 1,2-dichloroethane (1) + CCl_4 (2) (⊙) at 298.15 K (this work), (○) at 298.15 K (*14*), (□) at 303.15 K (*26*), (▽) at 293.15 K (*16*).

Comparison with DISQUAC Predictions

Chloroalkanes are regarded as consisting of two types of groups or contact surfaces: (i) type a—aliphatic (CH_3 or CH_2) and (ii) type d—chlorine (Cl).

Table V. DISQUAC Interchange Coefficients, Dispersive $C^{\mathrm{dis}}_{\mathrm{st},l}$ and Quasi-Chemical $C^{\mathrm{quac}}_{\mathrm{st},l}$ (l = 1, Gibbs Energy; l = 2, Enthalpy) for Contacts: a, CH_3 or CH_2; d, Cl in CCl_4; d′, Cl in 1-chloroalkanes; d″, Cl in 1,2-dichloroethane

s	t	$C^{\mathrm{dis}}_{\mathrm{st},1}$	$C^{\mathrm{dis}}_{\mathrm{st},2}$	$C^{\mathrm{quac}}_{\mathrm{st},1}$	$C^{\mathrm{quac}}_{\mathrm{st},2}$
a	d	0.093[a]	0.180[a]		
a	d′	0.093[a]	0.180[a]	2.34[a]	3.75[a]
a	d″	0.093[a]	0.180[a]	1.67[a]	3.20[a]
d	d′	1.70[b]	1.99[b]		
d	d″	1.08[b]	1.90[b]		
d′	d″	–0.013[c]	–0.12[c]		

[a] Reference 5. [b] Reference 4. [c] This work.

The aliphatic groups are assumed to exert the same force field independent of the *n*-alkane or chloroalkane.

In the chloroalkane mixtures under investigation, we distinguished three types of Cl atoms: d—in CCl_4, d′—in $CH_3(CH_2)_2CH_2Cl$, and d″—in $ClCH_2CH_2Cl$, each with a specific force field.

The relative volumes and surfaces of these groups and the related geometrical parameters of the molecules are listed in Table II of ref 5.

In DISQUAC, each (s,t) contact (s, t = a, d, d′, d″) is characterized by two dispersive interaction coefficients, $C^{\mathrm{dis}}_{\mathrm{st},l}$, and two quasichemical interaction coefficients, $C^{\mathrm{quac}}_{\mathrm{st},l}$, where l = 1, for the Gibbs energy parameter, and l = 2, for the enthalpy parameter.

The equations used to calculate G^E and H^E have been given in previous publications (e.g., ref 5) and need not be repeated here.

The four types of surfaces generate six types of (s,t) contact. We need, therefore, as many as 24 interaction coefficients to describe G^E and H^E of the investigated mixtures. Most of these coefficients have been determined previously, as will be shown below.

The twelve (a,d), (a,d′), and (a,d″) parameters (Table V) have been determined from accurate experimental G^E and H^E data for tetrachloromethane, 1-chloroalkane, or α,ω-dichloroalkane + *n*-alkane mixtures (*5*). DISQUAC describes the nonpolar CCl_4 + *n*-alkane mixtures in terms of the dispersive coefficients only, $C^{\mathrm{dis}}_{\mathrm{ad},1} = 0.093$ and $C^{\mathrm{dis}}_{\mathrm{ad},2} = 0.180$, with $C^{\mathrm{quac}}_{\mathrm{ad},l} = 0$ (l = 1, 2). The same dispersive coefficients have been used for the polar chloroalkanes. The relatively smaller quasi-chemical coefficients $C^{\mathrm{quac}}_{\mathrm{ad''},l}$ of $ClCH_2CH_2Cl$, compared to the coefficients $C^{\mathrm{quac}}_{\mathrm{ad'},l}$ of $CH_3(CH_2)_2CH_2Cl$, reflect the proximity effect of the Cl atoms in 1,2-dichloroethane.

The eight (d,d′) and (d,d″) parameters have been estimated with the limited amount of available experimental data on G^E and H^E of CCl_4 + 1-chloroalkane or + α,ω-dichloroalkane mixtures (*4*). As a matter of fact, we disposed of reliable H^E data only. No VLE data had been reported for CCl_4 + 1-chloroalkanes, and the VLE data sets published for CCl_4 + α,ω-dichloroalkane mixtures were found to yield rather discordant G^E values. The asymmetrical shape of the H^E vs x_1 curves could be well represented assuming that the four quasi-chemical coefficients are equal to zero. We adjusted the two dispersive enthalpic coefficients $C^{\mathrm{dis}}_{\mathrm{dd'},2}$ and $C^{\mathrm{dis}}_{\mathrm{dd''},2}$ and estimated the two dispersive Gibbs energy coefficients $C^{\mathrm{dis}}_{\mathrm{dd'},1}$ and $C^{\mathrm{dis}}_{\mathrm{dd''},1}$ from the general trend of the other DISQUAC coefficients (*4*). The calculated VLE diagrams and our experimental points are shown in Figure 3.

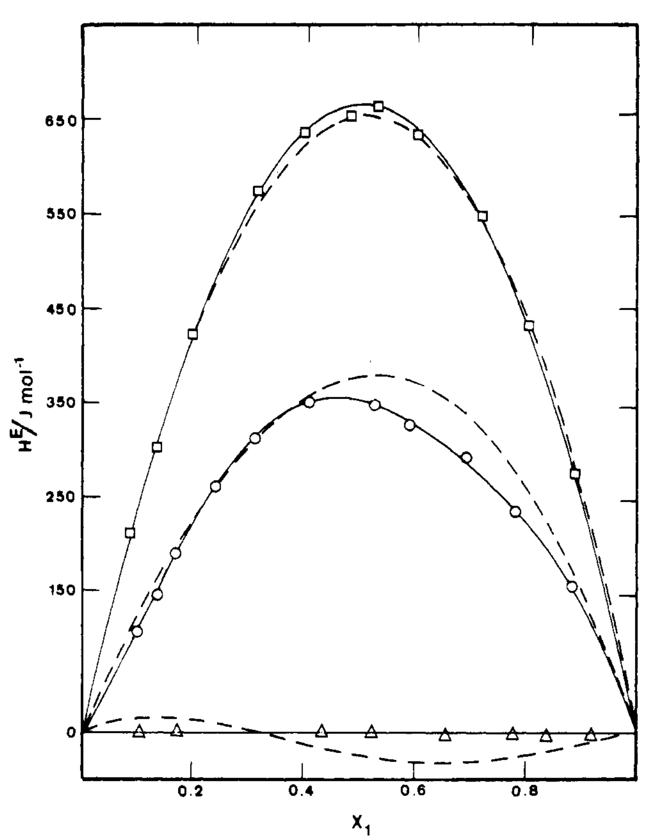

Figure 2. Excess molar enthalpies H^E at 313.15 K as a function of mole fraction x_1 (this work). Continuous curves, smoothed values, eq 1; dashed curves, DISQUAC predictions; points, direct experimental values: (○) 1,2-dichloroethane (1) + 1-chlorobutane (2), (□) 1,2-dichloroethane (1) + CCl_4 (2), (△) 1-chlorobutane (1) + CCl_4 (2).

The standard deviations in pressure, $\sigma(P)$, vapor-phase composition, $\sigma(y_1)$, and molar excess enthalpy, $\sigma(H^E)$,

$$\sigma(Q) = \sum(Q - Q_{\mathrm{calc}})^2/N \qquad (5)$$

where $Q = P$, y, or H^E, between experimental measurements and DISQUAC calculations using the parameters of Table V,

Table VI. Azeotropic Coordinates, Pressure P_{Az} and Composition $x_{1,\mathrm{Az}}$, and Standard Deviations in Pressure $\sigma(P)$, Vapor-Phase Composition $\sigma(y_1)$, and Molar Excess Enthalpy $\sigma(H^E)$, between Experimental Measurements and Redlich–Kister Fit (RK) *P*–*x* Reduction (All Points Weighted Equally) or DISQUAC Calculations (DQ)

	$P_{\mathrm{Az}}/(10^3$ Pa)		$x_{1,\mathrm{Az}}$		$\sigma(P)/(10^3$ Pa)		$\sigma(y_1)$		$\sigma(H^E)$/(J mol^{-1})	
T/K	RK	DQ	RK	DQ	RK	DQ	RK	DQ	RK	DQ
					1-Chlorobutane (1) + Tetrachloromethane (2)					
298.15									0.9[a]	5
313.15	28.55[b]	28.69	0.138[b]	0.177	0.011[b]	0.17	0.000 53[b]	0.0013	1.0[b]	21
					1,2-Dichloroethane (1) + Tetrachloromethane (2)					
298.15	15.73[c]	15.54	0.210[c]	0.177	0.020[c]	0.27			0.3[d]	5
303.15	19.81[e]	19.19	0.196[e]	0.196	0.036[e]	0.48				
313.15	29.20[b]	29.03	0.228[b]	0.203	0.0083[b]	0.19	0.00096[b]	0.0046	4.7[b]	10
	29.52[f]		0.214[f]		0.23[f]	0.32	0.028[f]	0.030		
					1,2-Dichloroethane (1) + 1-Chlorobutane (2)					
298.15									2.1[g]	3
313.15	no azeotrope[b]				0.029[b]	0.047	0.0017[b]	0.0010	3.7[b]	27

[a] Reference 22. [b] This work. [c] Reference 15. [d] Reference 23. [e] Reference 19. [f] Reference 20. [g] Reference 24.

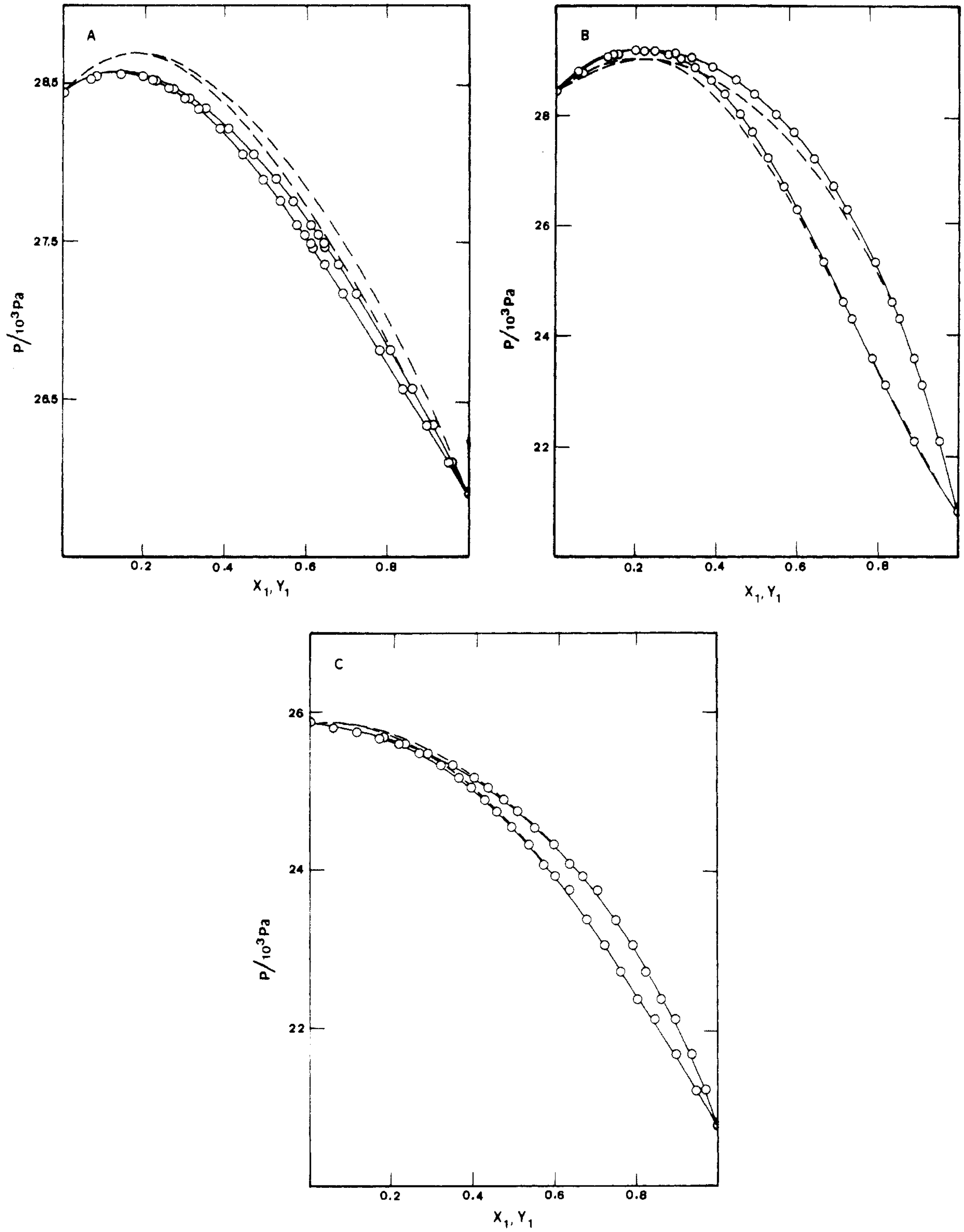

Figure 3. Vapor-liquid equilibrium diagrams at 313.15 K (this work). Pressure, P, as a function of mole fraction in liquid, x_1, or vapor, y_1, phase. Continuous curves, smoothed values; dashed curves, DISQUAC predictions; points, direct experimental values: (A) 1-chlorobutane (1) + CCl_4 (2); (B) 1,2-dichloroethane (1) + CCl_4 (2); (C) 1,2-dichloroethane (1) + 1-chlorobutane (2).

are presented in Table VI. For a better comparison, we have also listed the standard deviations obtained from the Redlich–Kister fit of the same experimental data, as well as the coordinates of the azeotropic points. These were determined by regression through minimization of the sum of the deviations in pressure, all points weighted equally. It can be seen that the DISQUAC predictions agree very well with our VLE measurements at 313.15 K (Figure 3A,B). It follows also that our measurements for 1,2-dichloroethane + CCl_4 are in good agreement with the VLE results of Azpiazu et al. (19), at 303.15 K, and of López et al. (*15*), at 298.15 K. There is also reasonable agreement between the data reported by Kireev and Skvortsova (*20*) and our data, at 313.15 K.

Finally, for the $ClCH_2CH_2Cl$ (1) + $CH_3(CH_2)_2CH_2Cl$ (2) mixture, we had to adjust the (d′,d″) contact parameters. We obtained again the best agreement with zero quasi-chemical coefficients. The dispersive coefficients $C^{\mathrm{dis}}_{\mathrm{d'd''},1}$ (Table V) are negative, indicating a somewhat stronger Cl–Cl interaction energy between the Cl groups of different types, than the average Cl–Cl interaction energy of the Cl groups of the same types. The standard deviations with DISQUAC are of the same order of magnitude as obtained with the Redlich–Kister fit (Table VI and Figure 3C).

There is excellent agreement between calculated and experimental H^E at 298.15 K. The $\sigma(H^E)$ values at 313.15 K are larger but still quite satisfactory (Figure 2).

Preliminary measurements and calculations for dichloromethane (CH_2Cl_2) + 1-chloroalkane mixtures show that the dispersive coefficients $C^{dis}_{d'd'',1}$ are more negative than for 1,2-dichloroethane + 1-chlorobutane. The parameters of the whole series of α,ω-dichloroalkane + 1-chloroalkane mixtures will be published in the near future.

Glossary

A_j	parameters in eqs 1 or 3
B_{ij}	molar second virial coefficients, $cm^3\ mol^{-1}$
C	interchange coefficient
G	molar Gibbs energy, $J\ mol^{-1}$
H	molar enthalpy, $J\ mol^{-1}$
m	number of parameters A_j, eqs 1 or 3
N	total number of measurements
n	number of C atoms in chloroalkane
P	total vapor pressure, Pa
Q	any property
R	molar gas constant (8.314 51 $J\ K^{-1}\ mol^{-1}$)
S	objective function, ref 12
T	temperature, K
V	liquid molar volume, $cm^3\ mol^{-1}$
WRMSD	weighted root mean square deviation, eq 4
x	liquid mole fraction
y	vapor mole fraction

Greek Letters

ρ	liquid density, $g\ cm^{-3}$
$\sigma(Q)$	standard deviation of property Q, eq 5
$\sigma_m(Q)$	standard deviation of property Q, eq 2
σ_e	experimental uncertainty

Superscripts

dis	dispersive term
E	excess property
quac	quasi-chemical term
°	pure component

Subscripts

Az	azeotropic property
calc	calculated property
i	type of molecule (component)
a, d, d′, d″	type of contact surface: a, aliphatic; d, Cl in CCl_4; d′, Cl in 1-chloroalkane; d″, Cl in 1,2-dichloroethane
l	order of interchange coefficient; l = 1, Gibbs energy; l = 2, enthalpy
s, t	any contact surface

Registry No. $CH_3(CH_2)_2CH_2Cl$, 109-69-3; CCl_4, 56-23-5; $ClCH_2CH_2Cl$, 107-06-2.

Literature Cited

(1) Kehiaian, H. V. *Pure Appl. Chem.* **1985**, *57*, 15.
(2) Garcia Vicente, I.; Garcia-Lisbona, N.; Velasco, I.; Otin, S.; Muñoz Embid, J.; Kehiaian, H. V. *Fluid Phase Equilib.* **1989**, *49*, 251.
(3) Wu, H. S.; Sandler, S. I. *AIChE J.* **1989**, *35*, 168.
(4) Kehiaian, H. V.; Marongiu, B. *Fluid Phase Equilib.* **1988**, *42*, 141.
(5) Kehiaian, H. V.; Marongiu, B. *Fluid Phase Equilib.* **1988**, *40*, 23.
(6) Berro, C.; Rogalski, M.; Péneloux, A. *Fluid Phase Equilib.* **1982**, *8*, 55.
(7) Berro, C.; Péneloux, A. *J. Chem. Eng. Data* **1984**, *29*, 206.
(8) Gutiérrez Losa, C.; Gracia, M. *Rev. Acad. Cienc. Exactas, Fis., Quim. Nat. Zaragoza* **1971**, *26*, 101.
(9) Velasco, I.; Otin, S.; Gutiérrez Losa, C. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1979**, 8.
(10) Marsh, K. N. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1973**, 22.
(11) Neau, E.; Péneloux, A. *Fluid Phase Equilib.* **1981**, *6*, 1.
(12) Fernández, J.; Berro, C.; Péneloux, A. *J. Chem. Eng. Data* **1987**, *32*, 17.
(13) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(14) Wilhelm, E.; Faradjzadeh, A.; Grolier, J.-P. E. *J. Chem. Thermodyn.* **1979**, *11*, 979.
(15) López, J. A.; Pérez, P.; Gracia, M.; Gutiérrez Losa, C. *J. Chem. Thermodyn.* **1988**, *20*, 447.
(16) Young, H. D.; Nelson, O. A. *Ind. Eng. Chem.* **1932**, *4*, 67.
(17) Sagnes, M.; Sánchez, V. *J. Chem. Eng. Data* **1971**, *16*, 351.
(18) Rathbone, P. Presented at the 4th International IUPAC Conference on Chemical Thermodynamics, Montpellier, France, August 26–30, 1975; Paper VI/II.
(19) Azpiazu, Y.; Royo, F.; Gutiérrez Losa, C. *J. Chem. Thermodyn.* **1984**, *16*, 561.
(20) Kireev, V. A.; Skvortsova, A. A. *Zh. Fiz. Khim.* **1936**, *7*, 63.
(21) TRC Thermodynamic Tables. Non-hydrocarbons. Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1973, d-7240 and k-7240; 1981, d-7242; 1981, d-7040 and k-7040 (loose-leaf data sheets).
(22) Marongiu, B. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1987**, 136.
(23) Marongiu, B. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1988**, 2.
(24) Muñoz Embid, J.; Roux, A. H.; Grolier, J.-P. E. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1990**, 59.
(25) Diguet, R.; Jadzyn, J. *J. Chem. Eng. Data* **1982**, *27*, 86.
(26) Vij, J. N.; Mahl, B. S. *Thermochim. Acta* **1975**, *12*, 155.

Received for review September 26, 1989. Accepted February 23, 1990. S.O. and J.M.E. are grateful for the financial assistance of the Dirección General de Politica Cientifica (Madrid, Spain) (PB 86-0184). J.M.E. greatly appreciates the financial assistance of the Ministère de la Recherche et de l'Enseignement Supérieur (France) and the Ministerio de Educación y Ciencia (Spain).

Solubility of Naphthalene in Mixtures of Carbon Dioxide and Ethane

William E. Hollar, Jr.,[†] **and Paul Ehrlich***

Department of Chemical Engineering, State University of New York at Buffalo, Amherst, New York 14260

The solubility of naphthalene in supercritical mixtures of carbon dioxide and ethane has been measured at temperatures of 308 and 318 K and over a pressure range of 50–300 atm with a static solubility apparatus. The resulting solubility data were correlated with the Chueh–Prausnitz modified version of the Redlich–Kwong equation of state.

I. Introduction

A number of authors have investigated the solubility behavior of solid solutes in contact with a binary solvent mixture that is supercritical at the conditions of the experiment (*1–3*). With the exception of one study (*1*), each has examined a polar or nonpolar liquid entrainer (cosolvent) at levels of 3–10 mol % as the second component of the supercritical solvent mixture. Schmitt and Reid (*1*) measured the solubility of naphthalene and benzoic acid in a mixture of 94% CO_2–6% C_2H_6 at 308 and 318 K. These data are the only source of information on the

---

[†] Present address: The Carborundum Co., P.O. Box 832, Niagara Falls, NY 14302.