

Measurements of VLE, h^E , and v^E for Binary Mixtures of Dibutyl Ether with 1-Chloropentane, 1,2-Dichloroethane, and 1,1,1-Trichloroethane

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Three binary systems of *d*-*n*-butyl ether with 1-chloropentane, 1,2-dichloroethane, and 1,1,1-trichloroethane were investigated first in a dynamic still, second in a flow calorimeter, and third in a densimeter. Vapor-liquid equilibria (VLE), excess enthalpies (h^E), and excess volumes (v^E) are reported at temperatures in the range of 283–370 K. With the results of the experiments, parameters of several "popular" expressions for the excess Gibbs energy are fitted with various fitting procedures. None of the g^E models and none of the fitting procedures is clearly superior to the others.

Introduction

Toward better understanding of the conditions in liquid mixtures it is helpful to have available a variety of experimental data. In addition, the experimental information can be used to determine molecular parameters, coefficients in empirical correlations, or coefficients in predictive correlations such as group-interaction models (1).

For the latter methods it is important to confirm or to improve the coefficients that characterize group-group interactions. For chlorinated hydrocarbons and ethers these interactions are sensitive to details of molecular structure.

Therefore, we report here experimental data for binary mixtures containing an ether and a hydrocarbon that is chlorinated once, twice, or three times (see Table I). This work is part of a long-term program (2, 3).

Experimental Section

Vapor-Liquid Equilibrium Apparatus. VLE experiments were performed in a dynamic still, Type Stage (4), with circulating liquid and vapor. Compared to other cells, this still offers the advantage of withdrawing liquid- and vapor-phase samples without interrupting the operation (see Figure 1). The temperature was determined with a calibrated 25- Ω platinum resistance thermometer (Rosemount 162 CE) in combination with a digital voltmeter and a thermostated 25- Ω standard resistance. The inaccuracy δT of the system was less than ± 0.01 K. A quartz Bourdon tube (Texas Instrument Model 145) pressure gauge with a sensitivity of 1 Pa and an indicating accuracy of ± 10 Pa was used to measure the system pressure. High vacuum (10^{-2} Pa) and atmospheric pressure read on a precision barometer served as reference pressures for the calibration. The pressure in the system was regulated within ± 5 Pa with an electric contact manometer actuating a solenoid valve. Pressure fluctuations were suppressed by a buffer volume of 50 dm³. The overall inaccuracy δp_1 in determining the system pressure is estimated to ± 15 Pa.

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Table I. Experimental Program

component		T/K		
1	2	VLE	h^E	v^E
C ₅ H ₁₁ Cl	C ₈ H ₁₈ O	313, 323	288, 298, 313	298
C ₂ H ₄ Cl ₂	C ₈ H ₁₈ O	330, 350, 370	288, 298	298
C ₂ H ₃ Cl ₃	C ₈ H ₁₈ O	323, 343	283, 298, 308	298

Table II. Properties of Pure Liquids: Density, Refractive Index and Normal Boiling Point at 101.325 kPa Determined in This Work Compared with Published Data

substance	$d(298.15 \text{ K}) / (\text{g}\cdot\text{cm}^{-3})$	$n_D(293.15 \text{ K})$	K
C ₈ H ₁₈ O	0.76425 ^a	1.3989 ^a	414.86 ^a
	0.7641 (8)	1.3992 (8)	415.12 (9)
	0.76461 (9)		415.4 (8)
C ₅ H ₁₁ Cl	0.87699 ^a	1.4139 ^a	381.08 ^a
	0.8769 (8)	1.4120 (8)	380.91 (10)
C ₂ H ₄ Cl ₂	1.24590 ^a	1.4448 ^a	356.63 ^a
	1.2458 (8)	1.4448 (8)	356.633 (8)
C ₂ H ₃ Cl ₃	1.32985 ^a	1.4372 ^a	347.20 ^a
	1.32998 (11)	1.4379 (8)	347.25 (11) 347.15 (8)

^aThis work.

Samples of the liquid and the condensed vapor were collected after steady-state operation and equilibrium was reached. The composition was determined by a gas chromatograph (GC, Hewlett Packard 5830 A) with a thermal conductivity detector calibrated with reference mixtures prepared gravimetrically. Each sample was analyzed at least three times. The precision of the analyzing instrument in mole fraction is ± 0.0002 .

Considering all inaccuracies in taking and handling the samples, the concentrations can be determined with an accuracy in mole fraction of $\delta x = 0.002$ in the liquid and of $\delta y = 0.003$ in the vapor.

Due to inaccuracies in the calibration procedure of each instrument, due to fluctuations in the operation of the still and due to error propagation for the interdependent variables, there will be a total uncertainty for each T, p, x, y point. The values of these uncertainties depend also on the properties of the mixture. For the systems investigated the uncertainty in pressure δp is calculated according to the error propagation formula; the values are given later in Table VII with the results of the consistency test.

Calorimeter. The heat of mixing was determined with a Picker flow calorimeter (5, 6). The principle of the measurement is shown in Figure 2. The calorimeter was operated for defined mixing ratios until the signal from the ΔT detector was indicating steady-state conditions. The temperature in the thermostat fluctuated less than ± 0.001 K. The Picker pumps were always operated with a constant total of the two flows $\dot{V}_1 + \dot{V}_2 = 0.013 \text{ cm}^3 \text{ s}^{-1}$. Fluctuations in the flow rate were less than $\pm 0.1\%$, and the inaccuracy of the ratio of the two flow rates at the same setting of the pumps was $\pm 0.01\%$. Measurements of the heat of mixing could be reproduced within $\pm 2\%$. The inaccuracy of the results is, therefore, expected

Table III. Parameters of the Antoine Equation (1) and Standard Deviations between Experimental and Correlated Vapor Pressures SIG(Dp) as well as Relative Deviations in Pressure Calculated by Using the Antoine Constants of this Work and of the Literature $D(AEQ)$, where $D(AEQ) = \int (AEQ_1 - AEQ_2)^2 dT^{0.5} / (T_{max} - T_{min})$

component	ref	$(T_{max} - T_{min})/K$	A	B	C	SIG(Dp)/kPa	$D(AEQ)/\%$
C ₈ H ₁₈ O	a	110	13.8340	3137.49	74.48	0.054	
	12	60	13.6341	2987.123	82.12		0.52
	8		14.8294	3795.581	43.15		0.44
C ₅ H ₁₁ Cl	a	86	13.9946	3037.315	57.15	0.031	
	10	25	16.0771	4356.491	0.0		0.91
	8	87	14.0252	3069.093	54.65		0.17
C ₂ H ₄ Cl ₂	a	59	14.1424	2896.480	52.51	0.011	
	13		14.5275	3127.970	40.95		0.05
	14	129	14.1614	2927.171	50.22		0.08
	15	29	14.1176	2882.031	53.27		0.08
C ₂ H ₃ Cl ₃	a	58	13.8574	2757.407	48.74	0.031	
	13		13.9876	2802.246	48.15		0.17

^aThis work.

Table IV. T, p, x, y Data and Relative Volatilities α_{12} for Coexisting Vapor and Liquid Phases of Binary Mixtures of Di-*n*-butyl Ether (2) with Three Chlorohydrocarbons

T/K	p/hPa	x_1	y_1	α_{12}	T/K	p/hPa	x_1	y_1	α_{12}	T/K	p/hPa	x_1	y_1	α_{12}
1-Chloropentane (1)					1,1,1-Trichloroethane (1)									
313.15	20.3	0.0000	0.0000		267.4	0.5424	0.9109	8.63		323.15	33.8	0.0000	0.0000	
	25.5	0.0774	0.2646	4.29	288.6	0.6096	0.9285	8.32		39.5	0.0141	0.1523	12.56	
	28.5	0.1209	0.3734	4.33	329.2	0.7350	0.9547	7.60		46.8	0.0335	0.2990	12.31	
	35.3	0.2242	0.5539	4.30	355.8	0.8277	0.9664	5.99		53.6	0.0517	0.4008	12.27	
	39.2	0.2877	0.6294	4.20	375.6	0.9060	0.9810	5.36		78.8	0.1152	0.6222	12.65	
	43.5	0.3549	0.6949	4.14	396.9	0.9700	0.9940	5.12		95.3	0.1575	0.7003	12.50	
	46.4	0.3978	0.7334	4.16	406.8	1.0000	1.0000			155.7	0.3082	0.8512	12.84	
	56.1	0.5515	0.8337	4.08	114.5	0.0000	0.0000			178.4	0.3613	0.8807	13.05	
	56.9	0.5678	0.8409	4.02	129.1	0.0163	0.1245	8.58		206.7	0.4270	0.9087	13.36	
	64.2	0.6810	0.8960	4.04	144.7	0.0340	0.2300	8.49		228.8	0.4821	0.9258	13.40	
	65.2	0.6964	0.9029	4.05	166.5	0.0578	0.3450	8.59		253.2	0.5367	0.9412	13.82	
	70.4	0.7793	0.9345	4.04	232.9	0.1382	0.5704	8.28		272.8	0.5861	0.9515	13.85	
	73.1	0.8225	0.9490	4.02	418.5	0.3671	0.8232	8.03		303.7	0.6558	0.9648	14.39	
	78.1	0.8985	0.9726	4.01	520.6	0.5069	0.8880	7.71		326.0	0.7065	0.9726	14.75	
80.1	0.9307	0.9817	3.99	577.6	0.5908	0.9144	7.40		352.1	0.7656	0.9804	15.31		
84.6	1.0000	1.0000		653.9	0.7080	0.9446	7.03		377.9	0.8271	0.9865	15.28		
323.15	34.1	0.0000	0.0000		693.1	0.7754	0.9571	6.46		397.4	0.8707	0.9906	15.65	
	40.7	0.0631	0.2131	4.02	725.3	0.8334	0.9668	5.82		432.6	0.9492	0.9968	16.67	
	48.5	0.1416	0.3951	3.96	754.2	0.8843	0.9774	5.66		434.5	0.9544	0.9971	16.43	
	60.9	0.2652	0.5870	3.94	773.8	0.9197	0.9830	5.05		442.6	0.9771	0.9986	16.72	
	69.3	0.3509	0.6786	3.91	783.0	0.9337	0.9862	5.07		451.2	1.0000	1.0000		
	76.8	0.4291	0.7436	3.86	803.0	0.9692	0.9931	4.57		86.3	0.0000	0.0000		
	88.0	0.5460	0.8207	3.81	808.1	0.9788	0.9953	4.59	343.15	114.4	0.0380	0.2724	9.48	
	93.3	0.5990	0.8507	3.81	815.7	0.9896	0.9976	4.37		155.2	0.0955	0.4976	9.38	
	95.4	0.6220	0.8614	3.78	820.3	1.0000	1.0000			203.2	0.1557	0.6440	9.81	
	98.7	0.6552	0.8779	3.78	1,2-Dichloroethane (1)					252.8	0.2194	0.7373	9.99	
	102.7	0.6952	0.8969	3.81	248.8	0.0000	0.0000			306.7	0.2889	0.8032	10.05	
	110.7	0.7789	0.9303	3.79	264.1	0.0097	0.0669	7.32		359.4	0.3538	0.8484	10.22	
	117.0	0.8443	0.9536	3.79	326.6	0.0502	0.2765	7.23		468.9	0.4870	0.9093	10.56	
	122.7	0.9042	0.9725	3.75	380.0	0.0842	0.3960	7.13		533.4	0.5616	0.9337	10.99	
126.8	0.9474	0.9855	3.77	473.3	0.1490	0.5530	7.07		535.3	0.5664	0.9344	10.90		
130.6	0.9860	0.9960	3.54	680.6	0.2902	0.7381	6.89		602.0	0.6444	0.9533	11.26		
131.9	1.0000	1.0000		758.1	0.3475	0.7836	6.80		650.8	0.7002	0.9639	11.43		
330.00	1,2-Dichloroethane (1)				828.5	0.3999	0.8171	6.70		673.1	0.7246	0.9684	11.65	
	47.9	0.0000	0.0000		902.3	0.4571	0.8491	6.68		739.1	0.7979	0.9798	12.29	
	64.8	0.0374	0.2877	10.40	957.8	0.5032	0.8692	6.56		792.7	0.8533	0.9872	13.26	
	79.2	0.0695	0.4376	10.42	1040.3	0.5690	0.8951	6.46		800.4	0.8665	0.9884	13.13	
	95.2	0.1046	0.5497	10.45	1119.2	0.6366	0.9162	6.24		822.3	0.8795	0.9898	13.30	
	103.5	0.1272	0.5959	10.12	1282.8	0.7851	0.9512	5.34		851.4	0.9223	0.9936	13.08	
	138.3	0.2073	0.7241	10.04	1357.5	0.8555	0.9666	4.89		870.7	0.9506	0.9962	13.62	
	191.5	0.3339	0.8308	9.80	1432.5	0.9259	0.9822	4.42		875.5	0.9631	0.9971	13.17	
	218.6	0.4304	0.8673	9.67	1505.2	0.9899	0.9975	4.07		884.1	0.9776	0.9983	13.46	
	248.0	0.4817	0.8948	9.15	1515.3	1.0000	1.0000			889.6	0.9904	0.9993	13.84	
										893.1	1.0000	1.0000		

to be $\pm 2\%$, provided complete mixing was assured. It was, however, sometimes difficult to accomplish complete mixing.

Densimeter. Densities of pure liquids and their mixtures were determined with two vibrating U-tube instruments, Type A.Paar (DMA 602/60), one filled with the gravimetrically prepared mixture and the other with a pure component as a ref-

erence (7). The temperature of the bath liquid was controlled within ± 0.01 K. The relative inaccuracy of the densities is 10^{-4} .

Pure Substances. The substances were purified according to recommendations of Riddick et al. (8). The ether was dried with sodium hydroxide and distilled at subatmospheric pressure in a high-efficiency spinning band column to remove peroxides

Table VI. Experimental v^E - x Data for Mixtures of Dibutyl Ether (2) with Three Chloroalkanes

T/K	x_1	$v^E/(cm^3 \cdot mol^{-1})$
1-Chloropentane (1)		
298.15	0.1741	-0.0586
	0.2114	-0.0640
	0.3910	-0.0874
	0.4076	-0.0882
	0.5141	-0.0930
	0.5766	0.0895
	0.6516	-0.0830
	0.7091	-0.0740
	0.7999	-0.0554
	0.8527	-0.0419
1,2-Dichloroethane (1)		
298.15	0.1972	0.0822
	0.4989	0.1977
	0.6100	0.2217
	0.6710	0.2197
	0.7083	0.2107
	0.7550	0.1946
0.8514	0.1581	
1,1,1-Trichloroethane (1)		
298.15	0.0154	-0.023
	0.0494	-0.060
	0.0971	-0.100
	0.1632	-0.220
	0.2389	-0.278
	0.4235	-0.368
	0.6555	-0.325
	0.8102	-0.247
	0.9226	-0.112
	0.9688	-0.045

por pressure as a function of temperature serves several purposes: (1) it provides a sensitive test for the purity of the substance if reliable published data are available for comparison; (2) after interpolation of the experimental points by a suitable formula such as the Antoine equation

$$\ln(p^{LV}/kPa) = A - B/(T/K - C) \quad (1)$$

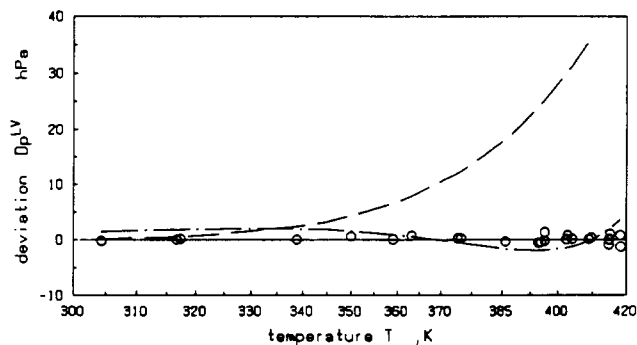
deviations between measured and calculated points provide an indication of the quality and reliability of the equipment; and (3) the pure-component vapor pressures must be known for reduction of binary data.

Table III lists, for all liquids, coefficients of the Antoine equation and integrated deviation in relative pressure between Antoine equations of this work and of literature (8, 10, 12-15). Figure 3 shows the deviations Dp between experimental pressure and calculated vapor pressures for dibutyl ether, using Antoine equation with coefficients fitted to the experimental data of this work and with coefficients reported in literature. The scatter of the experimental points gives a measure for the reproducibility of the data (vapor pressures were measured twice, once with increasing and once with decreasing temperature). There is a satisfactory agreement between our data and those of Riddick et al. (8).

Table VII. Results of the Consistency Test: Standard Deviations between Calculated and Observed Pressure SIG(Dp) and Average Absolute Deviation between Calculated and Observed Vapor Concentration AA(Dy) for Binary Mixtures of Dibutyl Ether with Three Chloroalkanes (the Degree of Legendre Polynomials is 3)

components	T/K	n^b	estd exptl $\delta p/kPa$	ideal gas		virial eq ^a	
				SIG(Dp)/ kPa	AA(Dy)	SIG(Dp)/ kPa	AA(Dy)
C ₅ H ₁₁ Cl	313.15	14	0.05	0.01	0.0012	0.01	0.0009
	323.15	15	0.06	0.01	0.0005	0.01	0.0008
C ₂ H ₄ Cl ₂	330.00	15	0.12	0.10	0.0018	0.10	0.0020
	350.00	16	0.21	0.10	0.0013	0.10	0.0024
	370.00	16	0.33	0.11	0.0015	0.11	0.0027
C ₂ H ₅ Cl ₃	323.15	19	0.13	0.10	0.0013	0.10	0.0025
	343.15	21	0.23	0.71	0.0032	0.72	0.0044

^a Second virial coefficients according to Hayden-O'Connell (17). ^b Number of experimental points.

**Figure 3. Deviations of the experimental vapor pressures (O) and values calculated from the Antoine equation of this work and from Antoine equations reported in literature: (---) Cydlinski (7) and (-.-) Riddick (17).**

Vapor-Liquid Equilibria. Temperature, pressure, and the mole fractions of liquid and vapor were measured in the equilibrium apparatus. Table IV presents all experimental data as well as the relative volatility α_{12} . Figures 4-6 show experimental bubble and dew points. For comparison, they also show the isotherms calculated from the Uniquac equation after adjustment of binary interaction parameters to the same set of binary data.

Excess Enthalpies. In the calorimeter, the heat of mixing (excess enthalpy) was determined for defined mixing ratios given by the volumetric flow rates of the two coupled Picker pumps. The composition of the mixture was checked by refractometry. Results are shown in Table V and in Figures 4-6.

Excess Volumes. Mixtures of two components were prepared gravimetrically by using a scale with an inaccuracy of ± 0.2 mg. The density of a pure liquid was determined (see Table II) after the instrument had been calibrated by the reference substances, i.e., distilled water and *n*-nonane (product of Fluka AG (CH) with a purity of better than 99.8%, GC). The densities of the mixtures were determined by differential measurements with one of the pure components as a reference. The differential method also reduced inaccuracies caused by temperature fluctuations in the circulating thermostat liquid. Experimental results are presented in Table VI.

Data Reduction

Consistency Test of VLE Data. In the test proposed by van Ness and Fredenslund (16), p - x data for one isotherm are used to fit the coefficients of a Legendre polynomial for g^E by minimizing the sum of the squares of the deviations between experimental pressure and calculated pressure. The degree of the polynomial should be considerably smaller than the number of experimental points. The standard deviation and a Dp vs. x plot provide an indication of the accuracy of the experimental method and of the reproducibility of the experimental data.

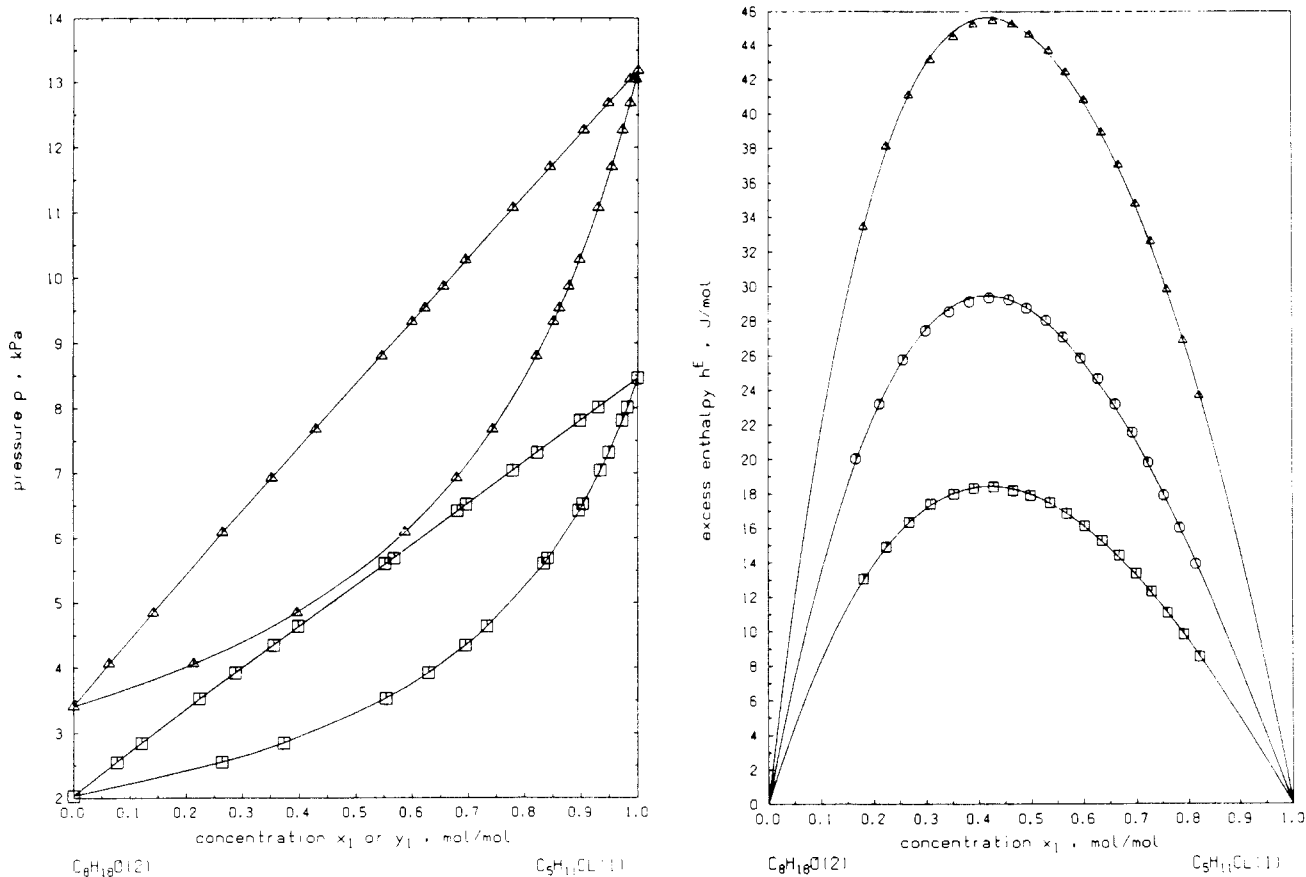


Figure 4. Experimental and calculated VLE and h^E for the system $C_6H_{11}Cl-C_8H_{18}O$. (Left) Experimental $p-x,y$ data; $T = 313.15$ K (\square) and $T = 323.15$ K (Δ); lines, Uniquac equation. (Right) Experimental h^E-x data; $T = 288.15$ K (\square), $T = 298.15$ K (\circ); and $T = 313.15$ K (Δ); lines, Redlich-Kister polynomials.

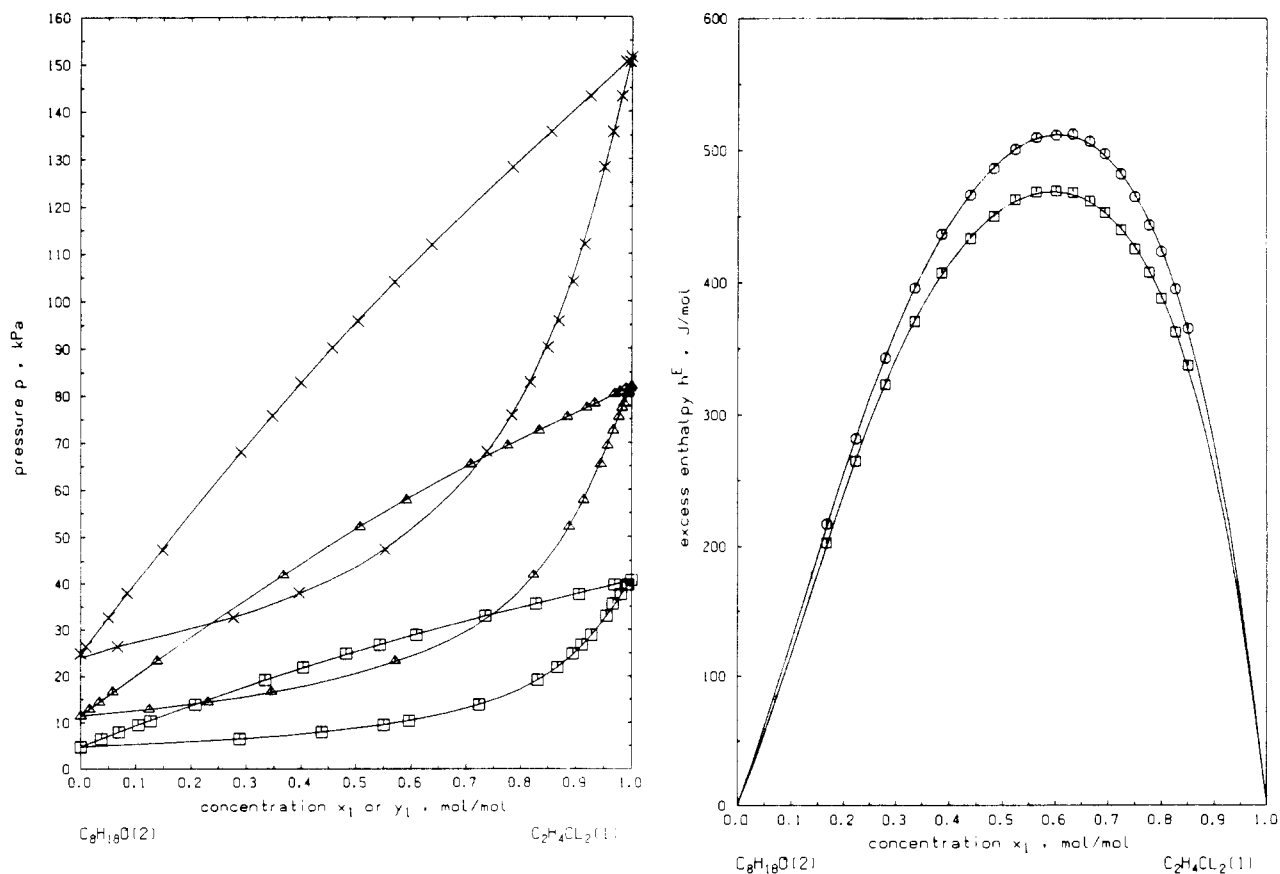


Figure 5. Experimental and calculated VLE and h^E for the system $C_2H_4Cl_2-C_8H_{18}O$. (Left) Experimental $p-x,y$ data; $T = 330.0$ K (\square), $T = 350.0$ K (Δ), and $T = 370.0$ K (\times); lines, Uniquac equation. (Right) Experimental h^E-x data; $T = 288.15$ K (\square) and $T = 298.15$ K (\circ); lines, Redlich-Kister polynomials.

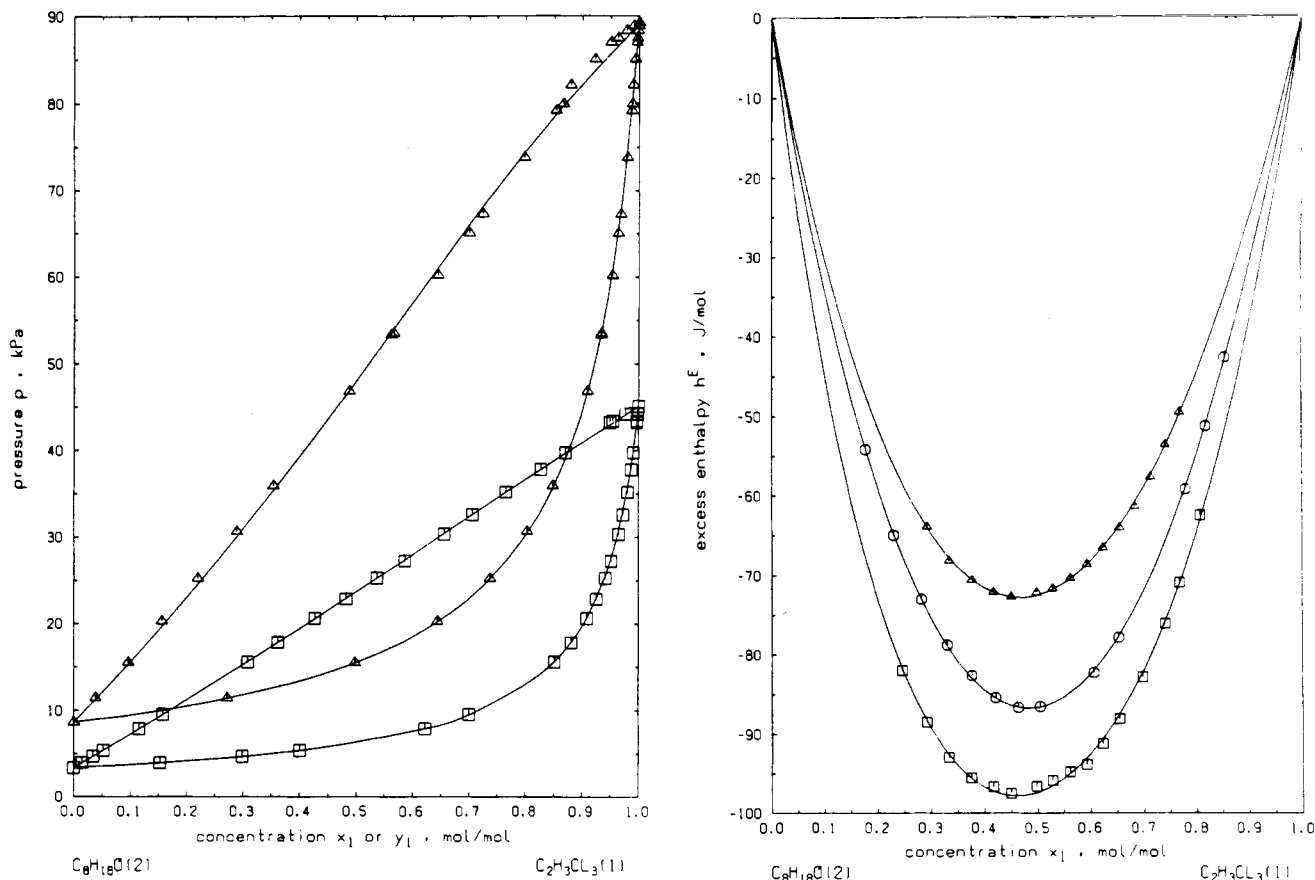


Figure 6. Experimental and calculated VLE and h^E for the system $C_2H_3Cl_3$ - $C_6H_{18}O$. (Left) Experimental p - x , y data; $T = 323.15$ K (\square) and $T = 343.15$ K (Δ); lines, Uniquac equation. (Right) Experimental h^E - x data; $T = 283.15$ K (\square), $T = 298.15$ K (\circ), and $T = 308.15$ K (Δ); lines, Redlich-Kister polynomials.

Table VIII. (A) Results of the Parameter Estimation Using the Algorithm of Prausnitz et al. (19), AP, and Kemeny et al. (21), KM, and (B) Comparison of Different Optimization Procedures and Objective Functions

A				B						
System 1: 1-Chloropentane-Dibutyl Ether				System: 1,2-Dichloroethane-Dibutyl Ether						
temp, K	313.15	323.15		T/K	model	RMS		parameters		method ^b
eq 20	Uniquac, AP	Van Laar, AP				D_p /kPa	D_y	X_{12}	X_{21}	
parameter ^a										
X_{12}	-865.12	0.0489		330	Uniquac	0.118	0.0021	457.92	31.42	KM
X_{21}	1103.64	0.0337				0.103	0.0020	350.63	128.11	BA
γ_1^∞	1.065	1.050				0.099	0.0022	209.16	268.69	AP
γ_2^∞	1.009	1.034			Margules-3	0.123	0.0031	0.3061	0.1405	KM
SIG(Dp)/kPa	0.007	0.009				0.108	0.0024	0.3195	0.1383	BA
SIG(Dp)	0.0014	0.0007				0.099	0.0033	0.3165	0.1557	AP
System 2: 1,2-Dichloroethane-Dibutyl Ether				350	Uniquac	0.101	0.0014	610.15	-98.70	KM
temp, K	330.0	350.0	370.0			0.120	0.0021	420.04	74.49	BA
eq 20	NRTL, KM	Van Laar, AP	Uniquac, AP			0.101	0.0014	605.26	-98.19	AP
parameter ^a					Margules-3	0.387	0.0039	0.3124	0.1952	KM
X_{12}	3988.24	0.1913	-5.75			0.361	0.0029	0.3060	0.1328	BA
X_{21}	-2041.01	0.5700	481.13			0.297	0.0037	0.2915	0.1822	AP
γ_1^∞	1.217	1.211	1.196	370	Uniquac	0.105	0.0019	2.69	472.21	KM
γ_2^∞	1.699	1.768	1.485			0.106	0.0019	6.62	467.99	BA
SIG(Dp)/kPa	0.084	0.083	0.105			0.359	0.0013	285.34	191.21	KM(b)
SIG(Dy)	0.0023	0.0018	0.0019			0.105	0.0019	-5.75	481.13	AP
System 3: 1,1,1-Trichloroethane-Dibutyl Ether					Margules-3	0.227	0.0021	0.2485	0.0964	KM
temp, K	323.15	343.15				0.231	0.0022	0.2532	0.0920	BA
eq 20	Uniquac, AP	Wilson, AP				0.598	0.0023	0.2727	0.1260	KM(b)
parameter ^a						0.203	0.0022	0.2482	0.1085	AP
X_{12}	842.50	-1708.26								
X_{21}	-692.43	5174.26								
γ_1^∞	0.914	0.846								
γ_2^∞	0.927	1.463								
SIG(Dp)/kPa	0.095	0.693								
SIG(Dy)	0.0014	0.0051								

^a Uniquac, NRTL, and Wilson parameters in $J \cdot mol^{-1}$; Third NRTL parameter $\alpha = 0.3$. ^b Methods: KM, maximum likelihood procedure with objective function $SSQ(Dp/p + \ln \gamma_1/\gamma_2)$; KM(b), minimizing the $SSQ(Dp/p + \ln \gamma_1/\gamma_2)$; BA, minimizing the $SSQ(Dp/p)$; AP, maximum likelihood procedure minimizing the weighted $SSQ(Dp + DT + Dx + Dy)$.

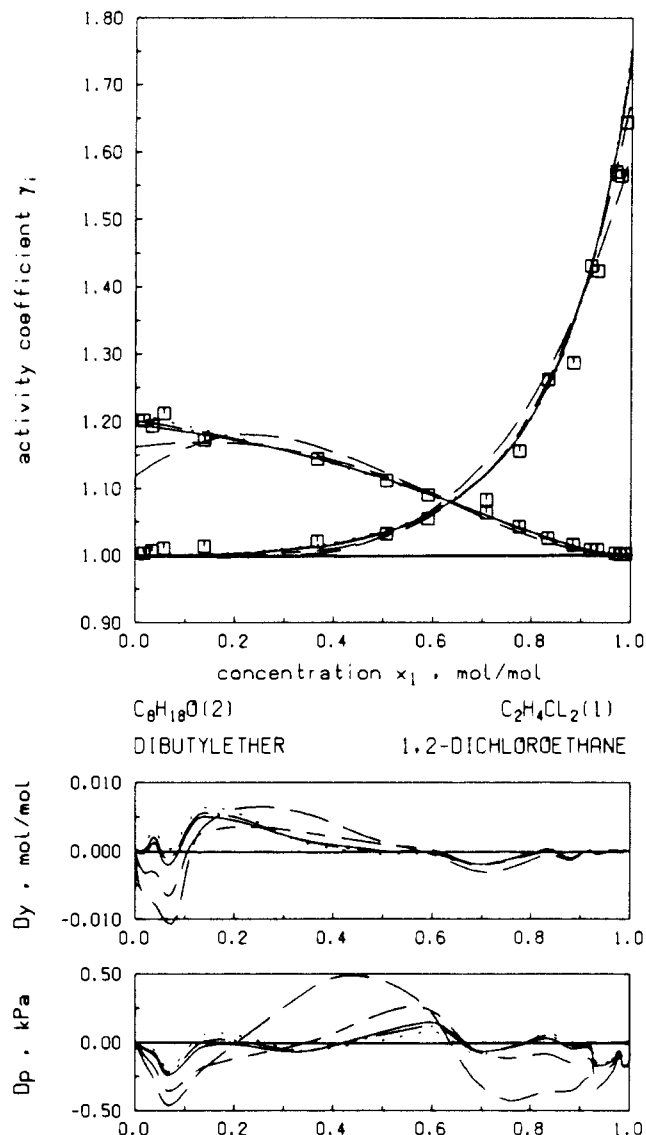


Figure 7. Activity coefficients γ_i vs. composition for the system $C_2H_4Cl_2$ - $C_8H_{18}O$ at $T = 350.0$ K. Experimental points and values calculated by several g^E models as well as deviations in pressure and vapor composition: (---) Margules, (···) Van Laar, (-·-) Wilson, (- - -) NRTL, (—) Uniquac.

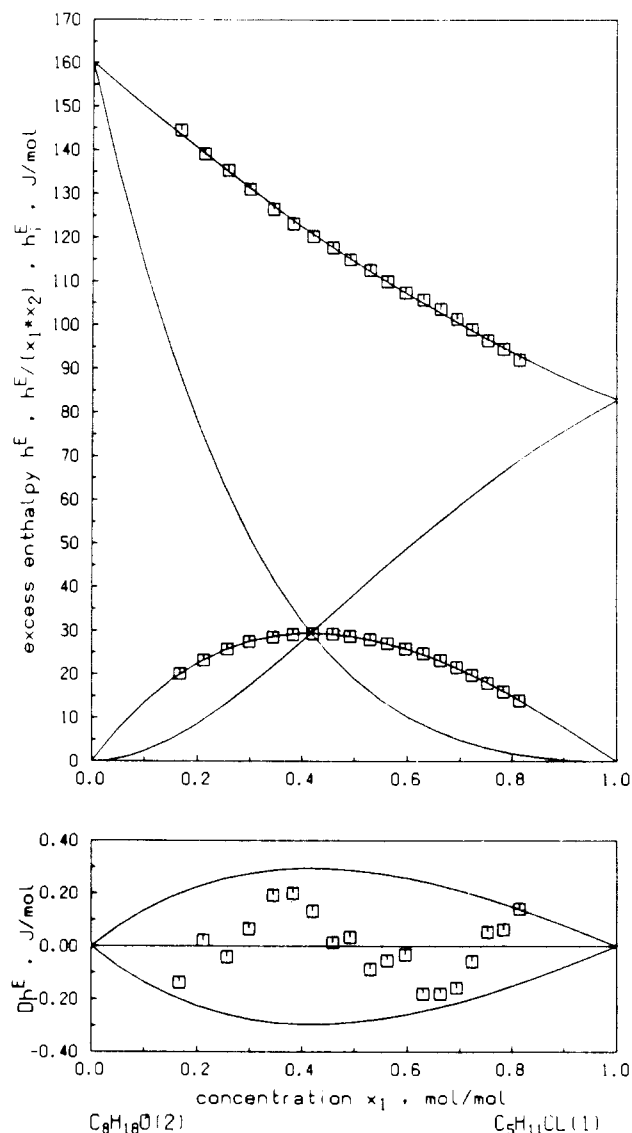


Figure 8. h^E , $h^E/(x_1x_2)$, and h_1^E, h_2^E vs. composition for the system $C_5H_{11}Cl$ - $C_8H_{18}O$ as well as the deviations Dh^E of the correlation with Redlich-Kister polynomial. Points: experimental data; lines: calculated by Redlich-Kister equation. The lens-shaped curve indicates 1% deviation.

Table IX. Coefficients of Eq 3, Standard Deviations, and Maximum Deviations for the h^E Measurements of Dibutyl Ether (2) with Three Chloroalkanes

component	T/K	A_1	A_2	A_3	A_4	SIG(Dh^E)/ ($J \cdot mol^{-1}$)	Dh^E_{max} / ($J \cdot mol^{-1}$)
$C_5H_{11}Cl$	288.15	71.9	-22.9	3.9		0.06	0.11
	298.15	114.7	-38.2	6.8		0.12	0.18
	313.15	178.5	-48.6	39.1		0.19	0.35
$C_2H_4Cl_2$	288.15	1825	546	394	674	1.35	3.19
	298.15	1975	690	423	554	1.63	2.91
$C_2H_3Cl_3$	283.15	-389.8	42.8	-115.7		0.53	0.81
	298.15	-346.6	20.6	-25.1		0.21	0.37
	308.15	-289.1	34.4	-29.3		0.26	0.51

Table X. Coefficients of Eq 3, Standard Deviations and Maximum Deviations for the v^E Measurements of Dibutyl Ether (2) with Three Chloroalkanes

component	T/K	A_1	A_2	A_3	SIG(Dv^E)/ ($cm^3 \cdot mol^{-1}$)	Dv^E / ($cm^3 \cdot mol^{-1}$)
$C_5H_{11}Cl$	298.15	-0.3680	0.0316	-0.0032	0.0018	0.0025
$C_2H_4Cl_2$	298.15	0.7968	0.5182	0.1015	0.0048	0.0066
$C_2H_3Cl_3$	298.15	-1.5244	-0.0798	0.0787	0.0165	0.0241

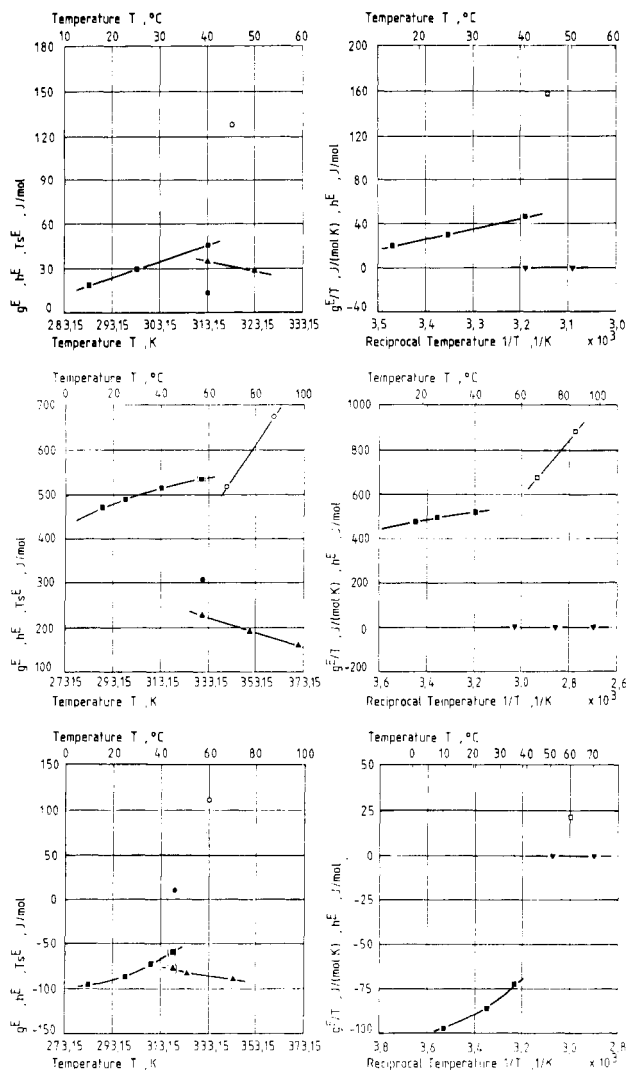


Figure 9. (a, top) Experimental h^E (■), g^E (▲), g^E/T (▼), and $Ts^E = h^E - g^E$ (●). Comparison with calculated calorific properties $Ts^E = -T(\partial g^E/\partial T)_{p,x}$ (○) and $h^E = (\partial(g^E/T)/\partial(1/T))_{p,x}$ (□) for the system $C_2H_4Cl_2-C_8H_{18}O$. (b, middle) The same as Figure 9a for the system $C_2H_4Cl_2-C_8H_{18}O$ (points in parentheses indicate extrapolated values). (c, bottom) The same as Figure 9a for the system $C_2H_3Cl_3-C_8H_{18}O$ (points in parentheses indicate extrapolated values).

The test was performed for ideal and for real gas behavior, although the real gas corrections were small. The truncated virial equation of state was used with second virial coefficients from Hayden and O'Connell (17). The Poynting correction is calculated assuming v_{01}^L to be independent of pressure. The liquid molar volume is calculated by the correlation of Hankinson et al. (18). The consistency can be checked by calculating vapor composition y^+ for each T, p, x point and by comparing y^+ with the experimental y . The absolute average deviation AA(Dy) and the Dy vs. x plot are indications of the consistency and most likely of the correctness of the data (see Table VII).

As the deviations AA(Dy) of the isotherms are approximately as large as the uncertainties of the experimental results, the T, p, x, y sets can be considered consistent. (The consistency was better for the assumption of ideal gas conditions.)

Only one isotherm (343.15 K) of the system 1,1,1-trichloroethane-dibutyl ether shows a noticeable deviation Dy. We observed by GC during the experiments an increasing amount of lighter impurities which could not be identified (probably due to chemical decomposition of the chloro compound).

Models for the Excess Gibbs Energy. Based on the experimental data and additional information about the thermo-physical properties, it is possible to determine the activity

coefficients for each experimental point with

$$\gamma_i(T, p, x_i) = \varphi_i^V p y_i / (x_i \varphi_{0i} p_{0i}^{LV} \exp[(v_{0i}^L/RT)(p - p_{0i}^{LV})]) \quad (2)$$

From the consistency test, it can be concluded that the vapor phase behaves ideally. Therefore, vapor-phase nonidealities are not considered.

An isothermal data set can be used to fit adjustable binary coefficients in so-called g^E models. Values of the coefficients and the SIG(Dp) and AA(Dy) are affected not only by the equation of state used for the vapor phase but also by the type of objective function used in the minimization procedure, by the minimizing algorithm itself, and by the choice of the subset chosen from the total set of experimental points.

It might help those who specialize in data reduction to learn about the results of parameter fitting. Therefore, a brief summary will be presented, without the intention to judge about the physical or chemical "truth" of the g^E models.

Table VIII, section B, gives a comparison of different optimization procedures for the system $C_2H_4Cl_2-C_8H_{18}O$. For the systems investigated it can be concluded, first, that for specified T and x , the p and y can be represented slightly better with the Uniquac model (with respect to the deviation RMS Dp and RMS Dy) than with the Margules equation independent of the fitting procedures; second, that for Uniquac the method suggested by Prausnitz and Anderson (19) yields the best set of parameters; third that the simplest procedure for minimizing the relative deviation in pressure (Dp/p) is as satisfactory as the more complicated and time-consuming procedures.

All experimental data sets were used to fit binary parameters for five popular g^E models (20) with the methods of Prausnitz (19) and Kemeny et al. (21). Table VIII, section A, gives the results of the parameter estimation for the model, which represents the data best.

In our experience there is no "favorite" model that could correlate the experimental data essentially better than the other models. As a typical example, Figure 7 gives the results for the $C_2H_4Cl_2-C_8H_{18}O$ system at 350 K, showing the activity coefficients calculated from the experimental data and values from several g^E models, as well as deviations in pressure and vapor concentration.

Redlich-Kister Polynomial for h^E . Experimental h^E-x data are usually correlated by a polynomial proposed by Redlich and Kister.

$$h^E = x_1 x_2 \sum (x_1 - x_2)^{k-1} A_k \quad k = 1, \dots, m \quad (3)$$

The degree $m - 1$ and the number of adjustable coefficients m depend on the complexity of the mixture. Table IX lists the coefficients of the isotherms for three binary systems. Figure 8 shows h^E , partial molar excess enthalpies, and $h^E/(x_1 \cdot x_2)$ calculated with the polynomial as well as experimental points. In addition, the deviations of single experimental points from the polynomial are plotted.

Data Reduction of v^E . Experimental values for the excess volumes were correlated by Redlich-Kister polynomials (eq 3). Table X gives coefficients of the correlation as well as standard and maximum deviations. In the $C_2H_3Cl_3-C_8H_{18}O$ system the accuracy of the experiments was lowered by the high relative volatility and by the large difference in density of pure components.

Consistency of VLE and h^E Data. If VLE and h^E measurements are performed at the same temperature, Ts^E can be determined. As vapor-liquid equilibria were investigated at several temperatures, g^E is known as a function of temperature. If h^E is also measured in the same temperature range, general thermodynamic relations can be used to compare the results of VLE and h^E experiments:

$$-T(\partial g^E/\partial T)_{p,x} = Ts^E = h^E - g^E \quad (4)$$

$$(\partial(g^E/T)/\partial(1/T))_{p,x} = h^E \quad (5)$$

The experiments in the calorimeter should preferably be performed at low vapor pressures of the solution; the dynamic VLE experiments are more accurate at higher vapor pressures. The experiments of phase equilibria and the caloric measurements are therefore not always made at exactly the same temperature. The results are graphically shown in Figure 9a-c at equimolar composition. In the g^E vs. T plot, the experimental $Ts^E = h^E - g^E$ is compared with Ts^E calculated from the slope of the g^E vs. T curve. In the g^E/T vs. $1/T$ plot the experimental h^E is compared with h^E calculated from the slope of the g^E/T vs. $1/T$ curve. The diagrams show that the temperature dependence of g^E or g^E/T based on VLE data is not of sufficient accuracy to allow prediction of h^E or Ts^E . As

$$h^E = (\partial(g^E/T)/\partial(1/T))_{p,x} = -T^2(\partial(g^E/T)/\partial T)_{p,x} \quad (6)$$

small inaccuracies in (g^E/T) are exaggerated by the large factor (T^2).

Conclusions. In addition to VLE, h^E and sometimes v^E measurements are necessary to obtain the complete information required for the design of industrial separation processes. If g^E is determined from VLE measurements, and if the change of g^E with temperature is calculated from two or three isothermal VLE experiments and if h^E is calculated with eq 6, the resulting value of h^E can be very inaccurate, especially if h^E is relatively small ($h^E < 500$ J/mol).

It can be concluded, therefore, that it is not satisfactory to find the temperature dependence of parameters in g^E models by evaluating VLE experiments only. Independent calorimetric experiments are required to give accurate information about the effect of temperature on activity coefficients.

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Glossary

A, B, C	Antoine constants
A_k	k^{th} coefficient of polynomial
d	density, g/cm ³
g	molar Gibbs energy, J/mol
h	molar enthalpy, J/mol
h_i	partial molar enthalpy, J/mol
m	number of adjustable parameters
n	number of experimental points
NBP	normal boiling temperature, K
n_D	refractive index
p	pressure, hPa, kPa
s	molar entropy, J/(mol K)
T	temperature, K
t	degree of polynomial
v	molar volume, cm ³ /mol
V	volume flow, cm ³ /s
X	parameter of g^E model
x	composition of liquid, mol/mol
y	composition of vapor, mol/mol
z	measurable quantity

δ	experimental uncertainty
φ	fugacity coefficient
γ	activity coefficient

Subscripts

i, j	component i, j
$0i$	pure component i (reference-state value)

Superscripts

E	excess quantity
L	liquid
V	vapor
$+$	calculated quantity

Other

α_{12}	relative volatility, $(y_1/x_1)/(y_2/x_2)$
Dz	deviation, $z - z^+$
AA(Dz)	absolute average deviation, $(1/n)\sum_i^n z - z^+ _i$
SIG(Dz)	standard deviation, $\{[1/(n-m)]\sum_i^n (z - z^+)_i^2\}^{0.5}$
RMS(Dz)	root mean square deviation, $[(1/n)\sum_i^n (z - z^+)_i^2]^{0.5}$

Registry No. C₈H₁₈O, 142-96-1; C₂H₄Cl₂, 107-06-2; C₂H₃Cl₃, 71-55-6; C₈H₁₁Cl, 543-59-9.

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