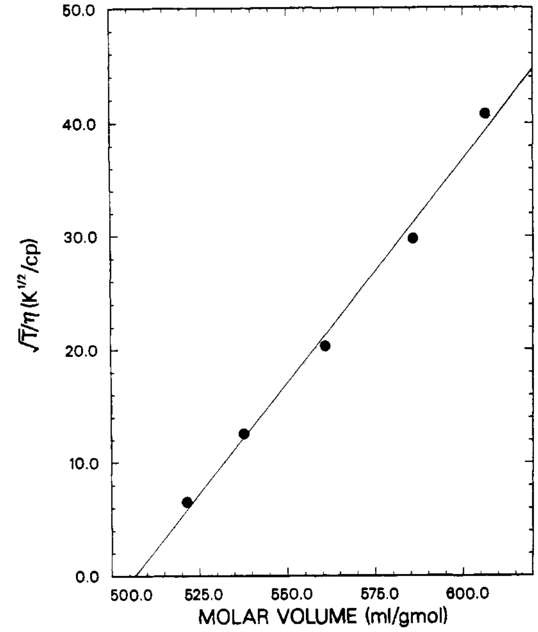

Figure 4. Dependence of $T^{1/2}/\eta$ on molar volume for *n*-octacosane.

L	dispersion tube length
$\dot{m}$	mass flow rate
M	mass of injected solute
r	dispersion tube radius
T	absolute temperature
$\bar{t}$	peak retention time
$\bar{u}$	average velocity of solvent
V	molar volume of solvent
V_t	total volume of dispersion tube
ρ	density
σ_1	solute hard-core diameter
η	viscosity

Registry No. H_2, 1333-74-0; CO, 630-08-0; CO_2, 124-38-9; n-C_8H_{18}, 111-65-9; n-$C_{12}H_{26}$, 112-40-3; n-$C_{16}H_{34}$, 544-76-3; n-$C_{28}H_{58}$, 630-02-4.

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Measurements of VLE, v^E, and h^E for Binary Mixtures of 1-Chlorohexane with Three *n*-Alkylbenzenes: Toluene, Ethylbenzene, *n*-Propylbenzene

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Results of a series of experimental investigations of three binary mixtures of 1-chlorohexane with toluene, ethylbenzene, and *n*-propylbenzene are reported: T, p, x, y data of vapor–liquid equilibria (VLE), h^E, T, x data of calorimetric measurements, and v, T, x data of volumetric measurements. VLE data are checked for thermodynamic consistency by performing the test of Fredenslund and used to fit parameters of several g^E models. UNIFAC predictions and experimental data are compared. h^E and v^E data were correlated with Redlich–Kister polynomials.

Introduction

Reliable experimental information, i.e., VLE, h^E, and v^E, is helpful to study and to understand the conditions in liquid mixtures. In addition, experimental data, particularly VLE, are of great importance for the thermodynamic design of industrial separation processes.

In continuation of the extensive experimental studies at our laboratories and in cooperation with the TOM project (*2*, *3*), mixtures of *n*-alkanes with chloroalkylbenzenes were investigated. A summary of the experimental program is given in Table I. The experimental data provide a basis to study heteroproximity effects of the functional groups of a molecule. For practical purposes experimental data can be represented by appropriate equations, i.e., VLE data by well-approved semitheoretical g^E models and h^E and v^E data with highly flexible Redlich–Kister polynomials.

Experimental Section

Apparatus and Instrumentation. (1) Vapor pressures of pure components and of mixtures were measured in a dynamic still, type Stage, with recycling liquid and vapor fractions. The temperature was determined with a platinum resistance thermometer, Pt 25 (Rosemount 162 CE), in combination with a standard resistor (25 Ω) and a six-digit voltmeter (Prema 6040,

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Table I. Experimental Program

component		T/K		
1	2	VLE	h^E	v^E
C_7H_8	$C_6H_{13}Cl$	323, 343	288, 298	288, 298
$C_6H_{13}Cl$	C_8H_{10}	323, 343	288, 298	288, 298
$C_6H_{13}Cl$	C_9H_{12}	363	288, 298	298

Table II. Sensitivity and Inaccuracy of Instruments and Systems

	VLE		
temperature	T, K	S[a]	0.0005
		I[a]	0.02
pressure	p, kPa	S	0.0005
		I	0.02
composition, liquid	x, mole fracn	S	0.0001
		I	0.001
composition, vapor	y, mole fracn	S	0.0001
		I	0.002
	h^E		
temperature	T, K	S	0.0005
		I	0.05
composition	x, mole fracn	S	
		I	0.004
excess enthalpy	h^E, J/mol	S	0.01
	$\Delta h^E/h^E$	I	0.04
	v^E		
temperature	T, K	S	0.01
		I	0.05
composition	x, mole fracn	S	0.00001
		I	0.0002
density	d, kg/m^3	S	0.001
		I	0.1
excess volume	v^E, cm^3/mol	S	0.0001
		I	0.05

[a] S = sensitivity of instruments or system; I = inaccuracy of the system, resulting from calibration, fluctuations, sample handling, etc.

Table III. Properties of Pure Liquids: Density (d), Refractive Index (n_D), and Normal Boiling Point (NBP) at 101.325 kPa Determined in This Work Compared with Published Data

substance	T/K	d/(g·cm^{-3})	n_D	NBP/K
C_7H_8	293.15	0.86691[a]	1.4969[a]	383.734[a]
		0.86696 (*14*)[b]	1.49693 (*14*)	383.775 (*14*)
C_8H_{10}	293.15	0.86693[a]	1.4957[a]	409.350[a,e]
		0.86702 (*14*)	1.49588 (*14*)	409.335 (*12*)
C_9H_{12}	293.15	0.86197[a]	1.4917[a]	(433.07)[a,c]
		0.8620 (*10*)	1.4920 (*10*)	432.367 (*18*)
$C_6H_{13}Cl$	293.15	0.87830[a]	1.4189[a]	408.222[a]
		0.8790 (*17*)		408.070 (*15*)
	298.15	0.87354[a]	1.4172[a]	
		0.8745 (*17*)		

[a] This work. [b] Numbers in parentheses are reference numbers. [c] Extrapolated.

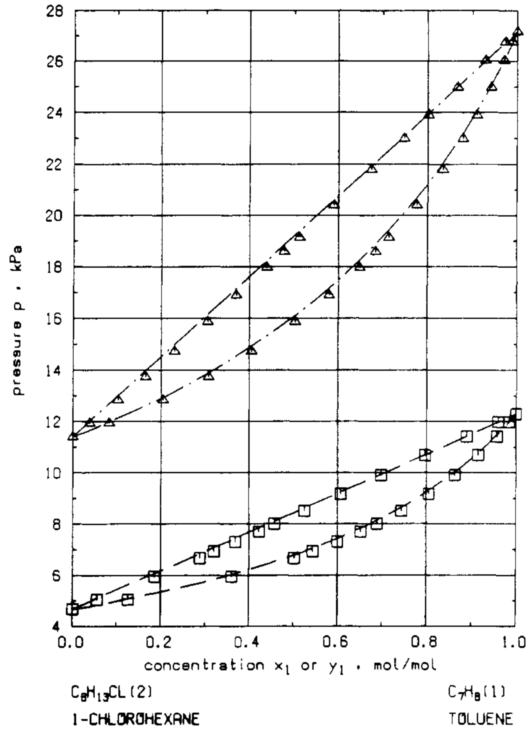

Figure 1. Experimental and calculated VLE for the system C_7H_8–$C_6H_{13}Cl$. Points, experimental p-x,y data, T = 323.15 K (□) and T = 343.15 K (△); lines, UNIFAC prediction.

FRG). A quartz Bourdon tube pressure gauge (Texas Instruments, Model 145) was used to measure the system pressure. The composition of the samples taken from the still was determined by a gas chromatograph (GC, Hewlett Packard 5830 A) with a thermal conductivity detector using 1.8-m columns with Apiezon M for the systems C_7H_8–$C_6H_{13}Cl$ and $C_6H_{13}Cl$–C_8H_{10} and with Apiezon L for the system $C_6H_{13}Cl$–C_9H_{12}. The GC was calibrated by reference mixtures prepared gravimetrically on a precision balance (Sartorius, FRG).

(2) Heats of mixing were measured in a flow calorimeter of type Picker manufactured by Setaram (France) (*4*). Table II shows a summary of the experimental inaccuracies of the instruments and apparatus. A detailed description of the experimental equipment and procedure is given in (*5*, *6*).

(3) Densities of pure components and of mixtures were measured in a vibrating tube densimeter, type A. Paar (DMA 602/60). Densities of the mixtures were determined in a differential arrangement of two cells, one filled with the gravimetrically prepared mixture and the other one of the pure components as a reference.

Table IV. Parameters of the Antoine Equation[a] and Standard Deviations between Experimental and Correlated Vapor Pressures SIG(Dp), as well as Relative Deviations in Pressure D(AEQ) Calculated by the Antoine Equation of This Work and of the Literature, D(AEQ) = $(\int(\mathrm{AEQ}_1 - \mathrm{AEQ}_2)^2\,dT)^{0.5}/(T_{max} - T_{min})$

compd	ref	$(T_{min} - T_{max})$/K	A	B	C	SIG(Dp)/kPa	D(AEQ)/%
C_7H_8	this work	300–338	14.0220	3107.20	53.311	0.06	
	12	308–384	13.9835	3101.06	53.457		0.40
	13	273–323	13.9494	3075.18	54.398		0.04
	14		13.9987	3096.52	53.668		0.02
C_8H_{10}	this work	320–400	13.9346	3232.67	62.358	0.01	
	12	329–410	14.0030	3277.83	60.059		0.02
	14		14.0045	3279.47	59.944		0.03
C_9H_{12}	this work	340–391	12.9827	2825.68	95.248	0.03	
	18	348–433	13.9972	3437.71	65.827		0.07
$C_6H_{13}Cl$	this work	319–376	13.8906	3166.40	66.719	0.01	
	15	288–409	14.2214	3365.73	57.584		0.03

[a] $\ln(p^{LV}/\mathrm{kPa}) = A - B/(T/\mathrm{K} - C)$.

Table V. T,p,x,y Data and Relative Volatilities α_{12} for Coexisting Vapor and Liquid Phases of Binary Mixtures of 1-Chlorohexane with Three Alkylbenzenes

p/kPa	x_1	y_1	α_{12}	p/kPa	x_1	y_1	α_{12}
			Toluene–1-Chlorohexane				
			T = 323.15 K				
4.68	0.0000	0.0000		8.51	0.5248	0.7441	2.63
5.05	0.0560	0.1261	2.43	9.17	0.6070	0.8056	2.68
5.95	0.1859	0.3615	2.48	9.90	0.6979	0.8635	2.74
6.68	0.2877	0.5015	2.49	10.69	0.7969	0.9156	2.76
6.93	0.3200	0.5434	2.53	11.40	0.8898	0.9575	2.79
7.31	0.3691	0.5995	2.56	11.97	0.9600	0.9854	2.81
7.69	0.4230	0.6519	2.55	12.28	1.0000	1.0000	
8.00	0.4578	0.6893	2.63				
			T = 343.15 K				
11.40	0.0000	0.0000		19.13	0.5129	0.7135	2.37
11.94	0.0389	0.0832	2.24	20.40	0.5900	0.7761	2.41
12.84	0.1029	0.2043	2.24	21.79	0.6739	0.8346	2.44
13.74	0.1647	0.3076	2.25	22.99	0.7464	0.8784	2.45
14.73	0.2306	0.4056	2.28	23.90	0.8017	0.9093	2.48
15.87	0.3046	0.5028	2.31	24.98	0.8666	0.9422	2.51
16.89	0.3707	0.5788	2.33	26.03	0.9288	0.9706	2.53
17.97	0.4388	0.6478	2.35	26.76	0.9731	0.9892	2.53
18.58	0.4783	0.6833	2.35	27.16	1.0000	1.0000	
			1-Chlorohexane–Ethylbenzene				
			T = 323.15 K				
4.65	0.0000	0.0000		4.59	0.4903	0.4891	1.00
4.64	0.0331	0.0322	0.97	4.59	0.5537	0.5535	1.00
4.63	0.0683	0.0664	0.97	4.60	0.5554	0.5554	1.00
4.62	0.1376	0.1345	0.97	4.59	0.6356	0.6370	1.01
4.61	0.2182	0.2141	0.98	4.60	0.7358	0.7388	1.02
4.60	0.3132	0.3093	0.98	4.61	0.8389	0.8420	1.02
4.60	0.3942	0.3914	0.99	4.63	0.9377	0.9396	1.03
4.59	0.4482	0.4460	0.99	4.64	0.9915	0.9918	1.04
4.59	0.4825	0.4811	0.99	4.64	1.0000	1.0000	
			T = 343.15 K				
11.26	0.0000	0.0000		11.24	0.4468	0.4477	1.00
11.25	0.0351	0.0342	0.97	11.24	0.4860	0.4876	1.01
11.25	0.1054	0.1044	0.99	11.24	0.4973	0.4990	1.01
11.24	0.1768	0.1758	0.99	11.25	0.5119	0.5140	1.01
11.24	0.2394	0.2387	1.00	11.25	0.5803	0.5830	1.01
11.24	0.3187	0.3182	1.00	11.28	0.7059	0.7097	1.02
11.24	0.3397	0.3395	1.00	11.31	0.8037	0.8075	1.02
11.24	0.3752	0.3754	1.00	11.34	0.9029	0.9055	1.03
11.24	0.3859	0.3861	1.00	11.37	0.9909	0.9912	1.03
11.24	0.4399	0.4410	1.00	11.38	1.0000	1.0000	
			1-Chlorohexane–n-Propylbenzene				
			T = 363.15 K				
11.32	0.0000	0.0000		18.46	0.5375	0.7106	2.11
11.87	0.0416	0.0758	1.89	19.58	0.6230	0.7775	2.11
13.71	0.1809	0.3169	2.10	20.69	0.7063	0.8350	2.10
14.65	0.2503	0.4151	2.13	21.83	0.7899	0.8898	2.15
15.67	0.3289	0.5096	2.12	23.04	0.8803	0.9402	2.14
16.78	0.4125	0.5979	2.12	24.06	0.9560	0.9789	2.14
17.32	0.4528	0.6366	2.12	24.65	1.0000	1.0000	
17.51	0.4699	0.6495	2.09				

Materials. The substances were obtained at high purity: $C_6H_{13}Cl$ and C_7H_6 from Fluka AG (Buchs, CH) in puriss. grade (>99% GC) and C_9H_{12} was purchased from Merck AG (FRG) ("zur Synthese" > 99% GC). In addition, all samples were thoroughly purified by vacuum distillation either in a 1-m packed column (2-mm glass helices) or a high-efficiency spinning band column. The chloroalkane was washed several times with concentrated sulfuric acid (12 h) and treated afterwards with dilute calcium chloride and distilled. The alkylbenzenes were dried with molecular sieves (4 Å) after distillation. Experimental work involving aliphatic chloroalkanes was done under an atmosphere of dry nitrogen and under protection from light. Pure chlorohexane was kept in refrigerated storage at 253 K.

The purification was complete when no secondary peaks were detectable by gas chromatographic analysis (GC); then three thermophysical properties, viz., density, refractive index, and normal boiling point, were measured and compared with literature data. The results are summarized in Table III.

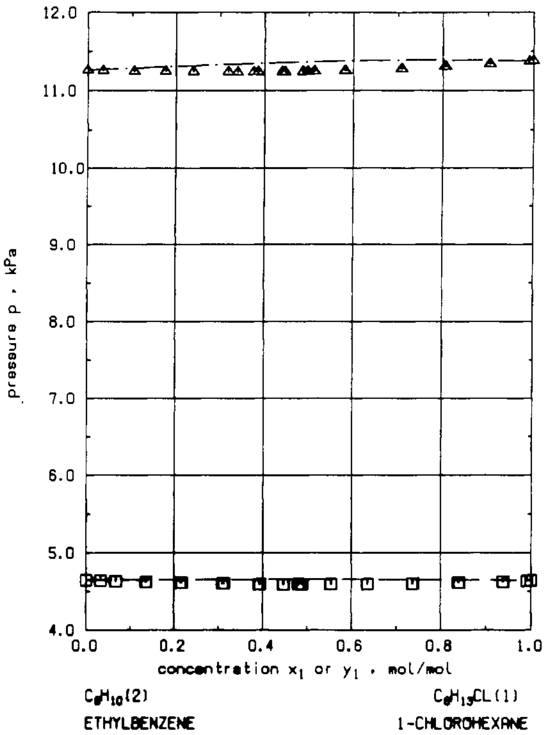

Figure 2. Experimental and calculated VLE for the system $C_6H_{13}Cl$–C_8H_{10}. Points, experimental p–x,y data, T = 323.15 K (□) and T = 343.15 K (△); lines, UNIFAC prediction.

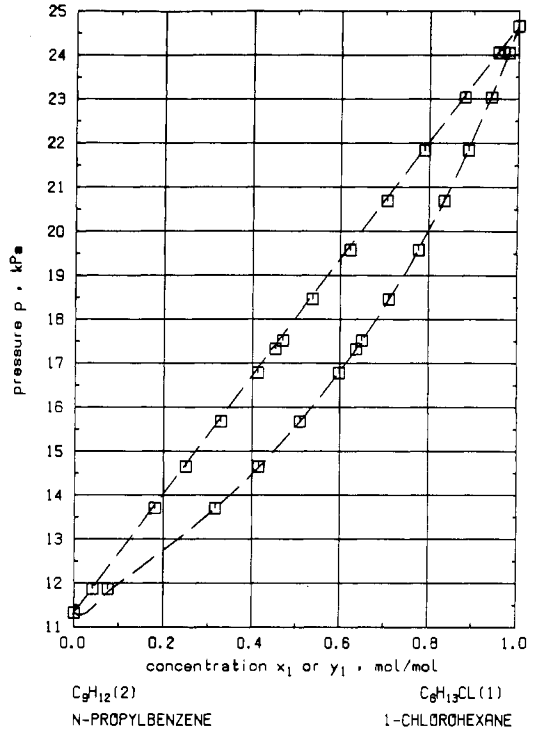

Figure 3. Experimental and calculated VLE for the system $C_6H_{13}Cl$–C_9H_{12}. Points, experimental p–x,y data, T = 363.15 K (□); lines, UNIFAC prediction.

Results

Vapor Pressure of Pure Liquids. Vapor pressures of all pure substances were measured in the range of 300 K < T < 400

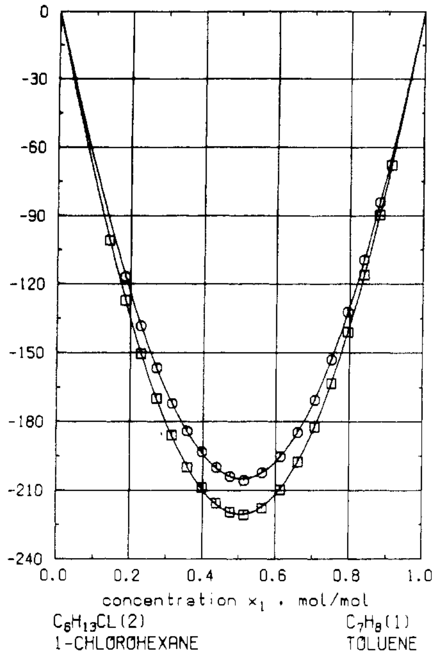

Figure 4. Experimental and calculated h^E data. Points: Experimental h^E for C_7H_8–$C_6H_{13}Cl$ at T = 288.15 K (□) and T = 298.15 K (○); lines represent the calculations of Redlich–Kister polynomials with parameters given in Table XI.

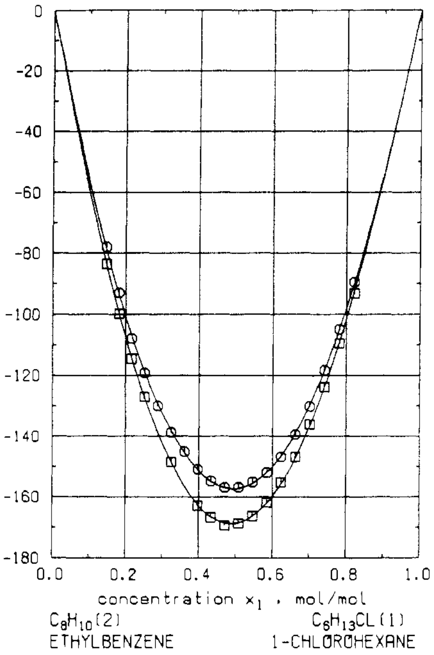

Figure 5. Experimental and calculated h^E data. Points: Experimental h^E for $C_6H_{13}Cl$–C_8H_{10} at T = 288.15 K (□) and T = 298.15 K (○); lines represent the calculations of Redlich–Kister polynomials with parameters given in Table XI.

K. The experimental data were used to determine the three parameters in Antoine's vapor pressure equation (with the maximum likelihood procedure described in ref 7). Antoine parameters based on our experiments and published by other authors are reported in Table IV. There is good agreement overall.

Vapor Liquid Equilibria. Experimental T, p, x, y data and corresponding relative volatilities α_{ij} for the mixtures are presented in Table V. Dew and bubble points and isotherms predicted with the UNIFAC model are shown in Figures 1–3.

Table VI. Experimental h^E–x Data for Mixtures of 1-Chlorohexane with Alkylbenzenes

x_1	h^E/ (J·mol^{-1})	x_1	h^E/ (J·mol^{-1})	x_1	h^E/ (J·mol^{-1})
Toluene–1-Chlorohexane					
T = 288.15 K					
0.1408	−100.9	0.4368	−215.6	0.7059	−182.4
0.1857	−127.2	0.4758	−219.6	0.7510	−163.4
0.2298	−150.5	0.5140	−220.7	0.7950	−141.0
0.2729	−169.9	0.5638	−217.8	0.8379	−116.1
0.3151	−186.0	0.6124	−209.8	0.8799	−89.6
0.3565	−200.0	0.6597	−197.7	0.9107	−67.9
0.3970	−208.7				
T = 298.15 K					
0.1857	−116.9	0.4368	−200.0	0.7059	−170.6
0.2298	−138.3	0.4758	−204.0	0.7510	−153.1
0.2729	−156.6	0.5140	−205.7	0.7950	−132.2
0.3151	−172.0	0.5638	−202.5	0.8379	−109.4
0.3565	−184.1	0.6124	−195.3	0.8799	−84.0
0.3970	−193.2	0.6597	−184.8		
1-Chlorohexane–Ethylbenzene					
T = 288.15 K					
0.1474	−83.6	0.4340	−166.7	0.6622	−146.9
0.1822	−99.8	0.4712	−169.3	0.7015	−136.2
0.2173	−114.6	0.5088	−168.7	0.7410	−123.9
0.2526	−127.1	0.5466	−166.3	0.7809	−109.6
0.3243	−148.5	0.5848	−161.9	0.8212	−93.2
0.3971	−162.9	0.6234	−155.2		
T = 298.15 K					
0.1474	−78.0	0.3971	−150.9	0.6234	−146.8
0.1822	−93.0	0.4340	−154.8	0.6622	−139.5
0.2173	−108.0	0.4712	−156.9	0.7015	−130.2
0.2526	−119.2	0.5088	−156.8	0.7410	−118.3
0.2883	−130.1	0.5466	−155.1	0.7809	−105.0
0.3243	−138.8	0.5848	−152.0	0.8212	−89.4
0.3605	−145.2				
1-Chlorohexane–n-Propylbenzene					
T = 288.15 K					
0.1266	−79.7	0.3909	−171.3	0.6532	−160.2
0.1644	−99.2	0.4285	−176.6	0.6905	−150.3
0.2023	−116.3	0.4660	−178.8	0.7278	−138.3
0.2401	−131.9	0.5035	−179.4	0.7651	−124.7
0.2778	−145.0	0.5410	−177.4	0.8023	−109.3
0.3156	−156.0	0.5785	−173.3	0.8394	−91.8
0.3532	−164.9	0.6159	−167.4		
T = 298.15 K					
0.1266	−70.6	0.3909	−160.3	0.6532	−149.0
0.1644	−87.9	0.4285	−165.0	0.6905	−140.4
0.2023	−104.5	0.4657	−168.3	0.7278	−128.1
0.2401	−119.8	0.5035	−169.3	0.7651	−115.1
0.2778	−133.5	0.5410	−167.0	0.8023	−100.2
0.3156	−144.3	0.5785	−163.0	0.8394	−84.3
0.3532	−153.2	0.6159	−156.7		

Excess Enthalpy Data. The results of h^E measurements are shown in Table VI and in Figures 4–6.

Excess Volume Data. The experimental v^E determined from the densities of the mixtures are presented in Table VII as well as in Figure 7.

Data Reduction

Consistency of VLE Data. With the redundant information of T, p, x, y data the consistency of the experimental results can be checked (provided vapor-phase behavior is known). In the present work the test of Fredenslund (*1*) was applied to the data. Vapor-phase imperfections were taken into account by using the virial equation of state truncated after the second term. Second virial coefficients of the pure components and

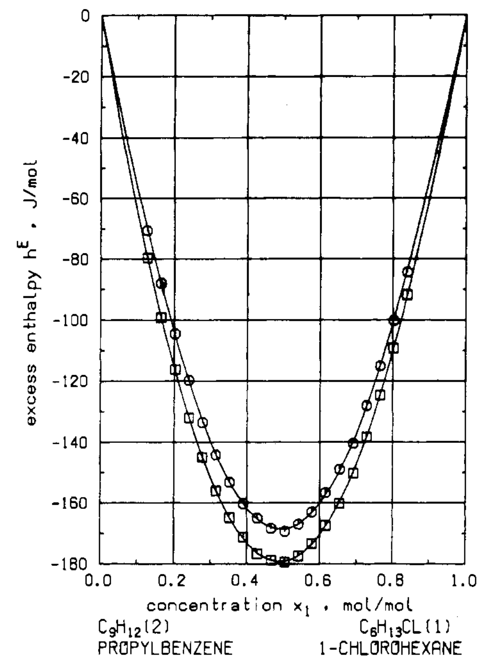

Figure 6. Experimental and calculated h^E data. Points: Experimental h^E for $C_6H_{13}Cl$–C_9H_{12} at T = 288.15 K (□) and T = 298.15 K (○); lines represent the calculations of Redlich–Kister polynomials with parameters given in Table XI.

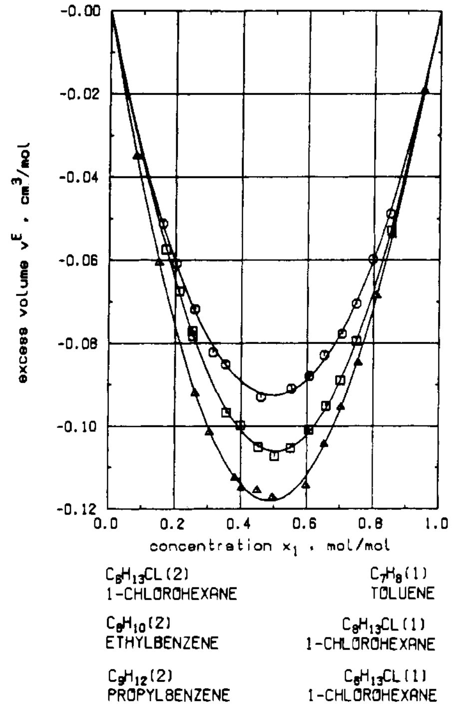

Figure 7. Experimental and calculated v^E data at T = 298.15 K. Points: Experimental v^E for C_7H_8 (1)–$C_6H_{13}Cl$ (2) (□) and for $C_6H_{13}Cl$ (1)–C_8H_{10} (2) (○) and for $C_6H_{13}Cl$ (1)–C_9H_{12} (2) (△). Lines represent the calculations of Redlich–Kister polynomials with parameters given in Table XII.

cross coefficients were calculated according to the correlation of Hayden et al. (*8*). The liquid molar volume $v_{0l}{}^L$ is calculated with the correlation of Hankinson (*9*) and the Poynting correction is calculated assuming $v_{0l}{}^L$ to be independent of pressure.

Fredenslund proposed as a criterion of consistency that the deviations in vapor concentrations AA(Dy) of experimental data and values calculated from Legendre polynomials should be less than 0.01 mol/mol. According to this criterion the VLE data presented in this study are consistent. The results of the

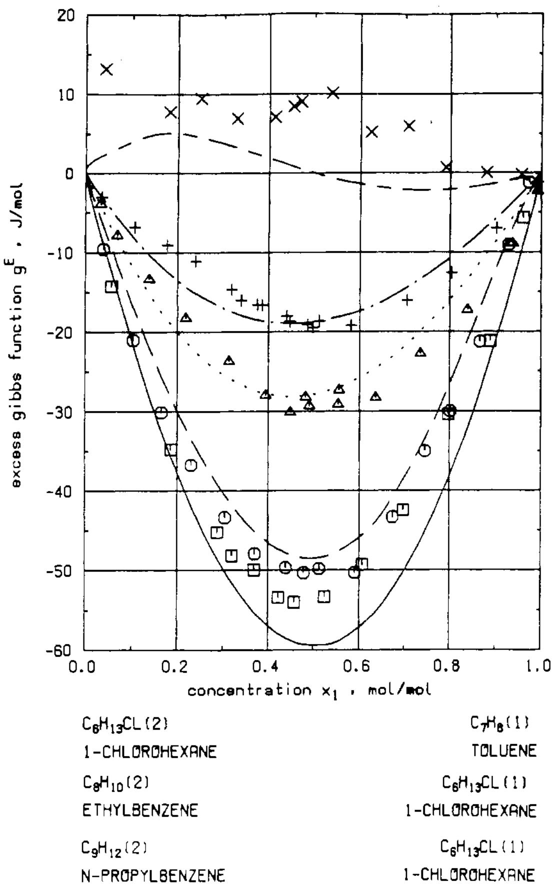

Figure 8. Experimental and calculated g^E vs composition. Points: Reduced experimental data for the system C_7H_8 (1)–$C_6H_{13}Cl$ (2) at T = 323.15 K (□) and T = 343.15 K (○), for the system $C_6H_{13}Cl$ (1)–C_8H_{10} (2) at T = 323.15 K (△) and T = 343.15 K (+), and for the system $C_6H_{13}Cl$ (1)–C_9H_{12} (2) at T = 363.15 K (×). Lines: Calculated values using the UNIQUAC equation with parameter obtained from the corresponding fit.

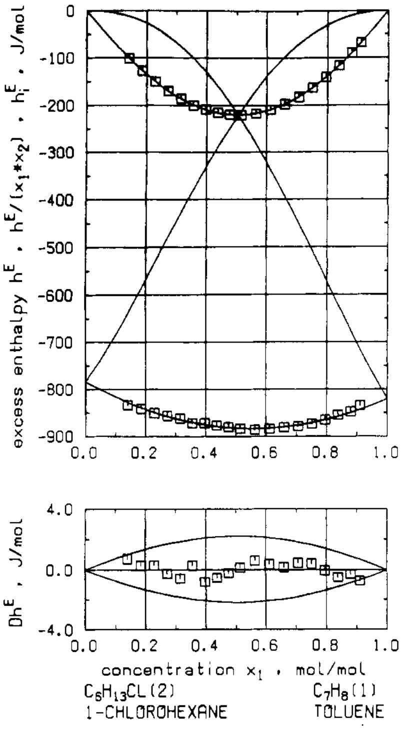

Figure 9. h^E, $h^E/(x_1x_2)$ and $h_1{}^E$, $h_2{}^E$ vs composition for the system C_7H_8–$C_6H_{13}Cl$ as well as the deviations Dh^E of the correlation with Redlich–Kister polynomial. Points: Experimental data at T = 288.15 K. Lines: Calculated by Redlich–Kister equation. The lens-shaped curve indicates 1% deviation.

Table VII. Experimental v^E–x Data for Mixtures of Chloroalkanes with Alkylbenzenes

x	v^E/ (cm^3·mol^{-1})	x	v^E/ (cm^3·mol^{-1})	x	v^E/ (cm^3·mol^{-1})
		Toluene–1-Chlorohexane			
		T = 288.15 K			
0.1940	−0.0616	0.4558	−0.1041	0.7193	−0.0832
0.3064	−0.0863	0.4659	−0.1045	0.7698	−0.0739
0.3317	−0.0920	0.5517	−0.1028	0.8010	−0.0648
0.3626	−0.0955	0.6023	−0.0992	0.8565	−0.0499
0.4003	−0.1011	0.6902	−0.0889		
		T = 298.15 K			
0.1707	−0.0574	0.3989	−0.0998	0.6579	−0.0951
0.2115	−0.0675	0.4522	−0.1051	0.7009	−0.0889
0.2533	−0.0783	0.5012	−0.1073	0.7490	−0.0795
0.2524	−0.0770	0.5499	−0.1053	0.8536	−0.0529
0.3559	−0.0967	0.6056	−0.1009		
		1-Chlorohexane–Ethylbenzene			
		T = 288.15 K			
0.1650	−0.0507	0.4040	−0.0904	0.6008	−0.0879
0.2003	−0.0608	0.4668	−0.0938	0.7601	−0.0666
0.2505	−0.0690	0.5156	−0.0942	0.8041	−0.0589
0.3208	−0.0830	0.5507	−0.0913	0.8514	−0.0452
0.3552	−0.0863				
		T = 298.15 K			
0.1616	−0.0512	0.4599	−0.0929	0.7067	−0.0777
0.2028	−0.0608	0.5523	−0.0909	0.7490	−0.0705
0.2606	−0.0718	0.6069	−0.0879	0.7978	−0.0598
0.3154	−0.0822	0.6515	−0.0829	0.8501	−0.0488
0.3537	−0.0851				
		1-Chlorohexane–n-Propylbenzene			
		T = 298.15 K			
0.0814	−0.0350	0.4036	−0.1149	0.7028	−0.0954
0.1504	−0.0606	0.4502	−0.1155	0.7545	−0.0847
0.2615	−0.0920	0.4970	−0.1172	0.8095	−0.0685
0.3062	−0.1015	0.5983	−0.1144	0.8551	−0.0540
0.3833	−0.1125	0.6529	−0.1044	0.9509	−0.0192

Table VIII. Results of the Consistency Test: Standard Deviation between Calculated and Observed Pressure SIG(Dp) and Average Absolute Deviation between Calculated and Observed Vapor Concentration AA(Dy) for Binary Mixtures of Alkylbenzenes with 1-Chlorohexane; Real Gas Behavior Calculated with the Virial Equation of State[a] (Degree of Legendre Polynomials = 3)[a]

			estimd exptl uncertainty			
binary system	T/K	exptl pts, n	δp/ kPa	δy	SIG(Dp)/ kPa	AA(Dy)
C_7H_8 (1)	323.15	13	0.04	0.0048	0.010	0.0009
	343.15	16	0.05	0.0031	0.013	0.0007
C_8H_{10} (2)	323.15	16	0.02	0.0058	0.002	0.0004
	343.15	18	0.03	0.0031	0.002	0.0002
C_9H_{12} (2)	363.15	13	0.05	0.0031	0.013	0.0029[b]

[a] Second virial coefficients according to Hayden–O'Connell (*8*). [b] The degree of Legendre polynomial is 1.

Table IX. Results of the Parameter Estimation Using the Algorithm of Prausnitz et al. (*14*)

System 1: Toluene (1)–1-Chlorohexane (2)		
temp, K	323.15	343.15
equation	NRTL	Wilson
parameter[a]		
X_{12}	2937.6	1811.0
X_{21}	-2369.3	-1812.9
$\gamma_{\infty 1}$	0.910	0.932
$\gamma_{\infty 2}$	0.946	0.959
SIG(Dp)/kPa	0.010	0.014
SIG(Dy)	0.001	0.001
System 2: 1-Chlorohexane (1)–Ethylbenzene (2)		
temp, K	323.15	343.15
equation	UNIQUAC	UNIQUAC
parameter[a]		
X_{12}	-1304.5	-1311.8
X_{21}	1605.10	1593.37
$\gamma_{\infty 1}$	0.965	0.979
$\gamma_{\infty 2}$	0.952	0.967
SIG(Dp)/kPa	0.004	0.002
SIG(Dy)	0.0003	0.0002
System 3: 1-Chlorohexane (1)–n-Propylbenzene (2)		
temp, K	363.15	
equation	NRTL	
parameter[a]		
X_{12}	-1718.0	
X_{21}	2078.9	
$\gamma_{\infty 1}$	1.014	
$\gamma_{\infty 2}$	0.991	
SIG(Dy)/kPa	0.015	
SIG(Dy)	0.0037	

[a] Parameters in J/mol (third NRTL parameter α = 0.3).

Table X. Comparison between Predictions of the UNIFAC Model[a] and the Experimental Data of the Present Work

system	T/K	RMS(Dp)/ kPa	AA(Dp/p)	RMS(Dy)/ mol fracn
C_7H_8–$C_6H_{13}Cl$	323.15	0.10	0.012	0.006
	343.15	0.20	0.011	0.005
$C_6H_{13}Cl$–C_8H_{10}	323.15	0.05	0.010	0.003
	343.15	0.09	0.008	0.003
$C_6H_{13}Cl$–C_9H_{12}	363.15	0.08	0.005	0.006

[a] Gas-phase nonidealities neglected.

Table XI. Coefficients of Eq 1, Standard Deviations, and Maximum Deviations for the h^E Measurements of 1-Chlorohexane with Three n-Alkylbenzenes

component	T/K	A_1	A_2	A_3	SIG(Dh^E)/ (J·mol^{-1})	Dh$^E_{max}$/ (J·mol^{-1})
C_7H_8 (1)	288.15	-882.3	-18.4	79.9	0.50	0.83
	298.15	-819.8	-32.4	76.2	0.40	0.72
C_8H_{10} (2)	288.15	-674.9	31.1	60.7	0.43	0.79
	298.15	-629.2	13.8	23.6	0.48	0.93
C_9H_{12} (2)	288.15	-716.8	27.3	31.5	0.25	0.45
	298.15	-674.2	15.5	91.8	0.46	0.81

consistency test and the uncertainties for pressure and vapor concentration calculated according to the error propagation formula are shown in Table VIII. It is evident that the estimated and the calculated uncertainties are in reasonable agreement.

***Models for the Excess Gibbs Energy*.** (1) For the practical application of VLE it is convenient to use g^E models for the representation of the experimental data and, to a limited degree, for extrapolation. Binary parameters of five two-parameter g^E models, viz., Margules-3, Van Laar, Wilson, NRTL, and UNIQUAC (*10*) were fitted by using the parameter estimation procedure of Prausnitz et al. (*11*). Since there is almost ideal mixing behavior, $|g^E| \leq 500$ J/mol, the differences of the fit using various g^E models are small. Table IX lists the results of the parameter optimization for the models which represent the data best. Figure 8 illustrates g^E calculated from experiment and g^E determined with the UNIQUAC equation by using parameters obtained from the fit. (2) A comparison between UNIFAC predictions of VLE using group interaction parameters from ref *1* and our new experimental data is given in Table X. It can be seen that predictions are of reasonable accuracy with

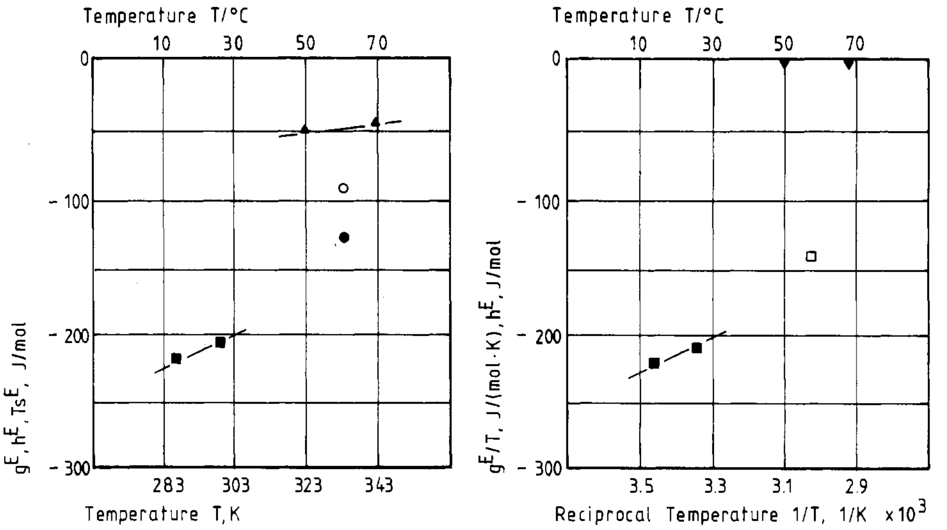

Figure 10. Experimental h^E (■), g^E (▲), and $Ts^E = h^E - g^E$ (●) for the system C_7H_8–$C_6H_{13}Cl$ at equimolar composition: comparison with calculated caloric properties Ts^E (○) and h^E (□).

Table XII. Coefficients of Eq 1, Standard Deviations, and Maximum Deviations for the v^E Measurements

component	T/K	A_1	A_2	A_3	SIG(Dv^E)/ ($cm \cdot mol^{-3}$)	Dv^E_{max}/ ($cm \cdot mol^{-3}$)
C_7H_8–$C_6H_{13}Cl$	288.15	−0.4191	−0.0096	0.0434	0.0008	0.0014
	298.15	−0.4238	−0.0132	0.0250	0.0007	0.0013
$C_6H_{13}Cl$–C_8H_{10}	288.15	−0.3745	0.0071	0.0154	0.0011	0.0015
	298.15	−0.3698	0.0018	−0.0190	0.0009	0.0016
$C_6H_{13}Cl$–C_9H_{12}	298.15	−0.4736	0.0258	0.0403	0.0011	0.0023

respect to the deviations in pressure and vapor-phase composition.

***Data Reduction* of h^E.** Experimental values for h^E of the binary system are correlated by Redlich–Kister polynomials. The results are shown in Table XI and in Figures 4–6. In addition, Figure 9 shows isotherms calculated with the polynomial for h^E, for the partial molar excess enthalpy h_i^E, and for $h^E/(x_1 \cdot x_2)$.

Data Reduction of v^E. Experimental values for v^E are correlated by a Redlich–Kister polynomial. The results are shown in Table XII and in Figure 7.

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.

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

and

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

The results at equimolar composition are graphically shown in Figure 10. The figure shows that there is qualitative agreement between experimental caloric data and h^E calculated from VLE. As has been pointed out previously by the authors (*5*, *6*), h^E cannot reliably (quantitatively) be predicted from the temperature dependence of g^E.

Summary

VLE, v^E, and h^E were measured for three binary mixtures of chlorohexane with *n*-alkylbenzenes. The systems show almost ideal mixing behavior; this is an interesting observation considering the strongly positive interactions of alkanes with chloroalkyl benzenes (*16*). The experimental data can be correlated with satisfying accuracy by using g^E models for VLE, and a Redlich–Kister expansion for v^E and h^E data. The experimental results are a contribution to the study on heteroproximity effects which is currently underway.

Acknowledgment

We express our appreciation for the effective help of Ms. C. Eichenauer in the laboratory.

Glossary

A, B, C	Antoine constants
A_k	kth coefficient of polynomial
c_p	heat capacity, J/(mol·K)
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
X	parameter of g^E model
x	composition of liquid, mol/mol
y	composition of vapor, mol/mol
z	measurable quantity

Greek Letters

α_{12}	relative volatility $(y_1/x_1)/(y_2/x_2)$
δ	experimental uncertainty
φ	fugacity coefficient
γ	activity coefficient

Subscripts

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

Superscripts

E	excess quantity
L	liquid
V	vapor
+	calculated quantity

Operators

Dz	deviation, $z - z^+$
AA(Dz)	absolute average deviation, $(1/n)\sum_i^n\lvert z - z^+\rvert_i$
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. 1-Chlorohexane, 544-10-5; toluene, 108-88-3; ethylbenzene, 100-41-4; *n*-propylbenzene, 103-65-1.

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Measurements of the Viscosities of Compressed Fluid and Liquid Carbon Dioxide + Ethane Mixtures

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The shear viscosity coefficients of three compressed fluid and liquid carbon dioxide + ethane mixtures have been measured with a torsional piezoelectric crystal viscometer at temperatures between 210 and 320 K and at pressures to about 30 MPa (4350 psi). The experimental error is estimated to be smaller than 3% in most cases. The measurements have been compared with an extended corresponding states model and have been used to examine the dependences of the fluidities (reciprocal viscosities) on molar volume and composition.

Introduction

Mixtures of carbon dioxide with hydrocarbons are of considerable interest for natural gas processing and for enhanced oil recovery research. Carbon dioxide is an unusual molecule as it has a large quadrupole moment, but no dipole moment. Although viscosities have been measured for both pure carbon dioxide (*1*) and pure ethane (*2*), we are not aware of any published viscosity data for their mixtures.

Apparatus and Procedures

The measurement method, apparatus, and procedures are essentially the same as we have used for our work on pure ethane (*2*) and on pure carbon dioxide (*1*). The same torsional piezoelectric quartz crystal of about 5 cm length and 0.5 cm diameter discussed in ref *3* was used for these measurements. Viscosities were derived from measured resonance curve bandwidths by using the equation (*4*)

$$\eta = \frac{\pi f}{\rho}\left[\frac{M}{S}\right]^2\left[\frac{\Delta f}{f} - \frac{\Delta f_{\text{vac}}}{f_{\text{vac}}}\right]^2 \tag{1}$$

where ρ is the fluid density, M is the mass, S is the surface area of the crystal, f is the resonant frequency, and Δf is the resonance-curve bandwidth of the crystal, measured at one-half of the conductance at resonance. The frequencies, f_{vac} and Δf_{vac}, are measured with the cell evacuated. The difference between f and f_{vac} is usually negligible.

Table I. Carbon Dioxide + Ethane Mixture Compositions

mixture	carbon dioxide, mole fraction	ethane, mole fraction
1	0.49245	0.50755
2	0.25166	0.74834
3	0.73978	0.26022

The gas mixture compositions, prepared gravimetrically from research grade carbon dioxide and research grade ethane, are summarized in Table I.

Chromatographic tests on the pure components showed that total impurities were below the 0.01% level for both gases. The errors in the mixture compositions are estimated to be smaller than 0.01%.

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