Thermochimica Acta, 108 (1986) 9–27
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MEASUREMENTS OF VLE, h^E AND v^E FOR BINARY MIXTURES OF n-ALKANES WITH n-ALKYLBENZENES

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(Received 2 April 1986)

ABSTRACT

As part of a long-term program, binary systems of n-alkanes: heptane, octane and nonane, with n-alkylbenzenes: ethylbenzene and propylbenzene, were investigated first in a dynamic still, second in a flow calorimeter and third in a densimeter. Experimental results are reported for vapor–liquid equilibria (VLE), excess enthalpies (h^E) and excess volumes (v^E).

Based on the T, p, x, y data sets, parameters in several "popular" expressions for the excess Gibbs energy are fitted with a maximum likelihood procedure.

INTRODUCTION

To improve our knowledge of the conditions in liquid mixtures, a variety of experimental data: VLE, h^E, v^E, are helpful. In addition, experimental information can be used either to determine molecular parameters, coefficients in empirical correlations or coefficients in predictive correlations, such as group-interaction models [1]. For the last methods it is important to confirm or to improve the coefficients that characterize group–group interactions. Obviously, these interactions are sensitive to details of molecular structure.

Therefore, we report here experimental data for binary mixtures containing n-alkanes and two n-alkylbenzenes (see Table 1). This study is part of a long-term program [3–5], the TOM project, and it is carried out in cooperation with Prof. Kehiaian [6,7].

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TABLE 1

Experimental program

(1) Vapor pressures of pure liquids

Component	$T_{min} - T_{max}$ (K)	$p_{min} - p_{max}$ (kPa)
C_8H_{18}	295–402	1.5–111.0
C_9H_{20}	322–413	5.6– 75.7
C_8H_{10}	320–400	4.0– 78.3
C_9H_{12}	340–391	4.2– 30.8

(2) VLE, h^E and v^E

Component		Temperature (K)		
1	2	VLE	h^E	v^E
C_7H_{16}	C_8H_{10}	– [a]	288, 308	298
C_8H_{10}	C_9H_{20}	333, 348, 363	–	293
C_8H_{18}	C_9H_{12}	343	298, 308	293, 298
C_9H_{20}	C_9H_{12}	353, 363	–	293

[a] Investigated by Myers (1955) [2].

EXPERIMENTAL EQUIPMENT

Vapor–liquid equilibrium apparatus

VLE experiments were performed in a dynamic still, of the Stage type [8], with circulating liquid and vapor. The temperature was determined with a calibrated 25 Ω platinum resistance thermometer (Rosemount 162 CE, U.S.A.) in combination with a digital voltmeter and a thermostated 25 Ω standard resistance. A quartz Bourdon tube pressure gauge (Texas Instrument model 145, U.S.A.) 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 using an electric contact manometer actuating a solenoid valve. Pressure fluctuations were suppressed by a buffer volume of 50 dm^3. 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, U.S.A.) with a thermal conductivity detector equipped with columns of polyethylene glycol (Carbowax 1500) for the ethylbenzene–nonane system, Apiezon M for nonane–propylbenzene (both at 373 K) and octane–propylbenzene (at 403 K). The analysis was calibrated with at least ten reference mixtures prepared gravimetrically. Each sample was analyzed three times. Further details of the apparatus and experimental procedure are given in refs. 3, 5 and 9. The experimental uncertainties are listed in Table 2.

TABLE 2

Sensitivity and inaccuracy of instruments and systems

Quantity	S[a]	I[b]
VLE		
Temperature, $T/(\mathrm{K})$	0.0005	0.02
Pressure, p (kPa)	0.0005	0.02
Composition, liquid, x (mol mol^{-1})	0.00001	0.001
vapor, y (mol mol^{-1})	0.00001	0.002
h^E		
Temperature, T (K)	0.0005	0.05
Composition, x (mol mol^{-1})	–	0.004
Excess enthalpy, h^E (J mol^{-1}) $\Delta h^E/h^E$	0.01	0.04
v^E		
Temperature, T (K)	0.01	0.05
Composition, x (mol mol^{-1})	0.00001	0.0002
Density, d (kg m^{-3})	0.001	0.1
Excess volume, v^E (cm^3 mol^{-1})	0.0001	0.01

[a] S = sensitivity of instruments or system.

[b] I = inaccuracy of the system, resulting from calibration, fluctuations, sample handling, etc.

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 also depend on the properties of the mixture. For the systems investigated the uncertainty in pressure, δp, and vapor concentration, δy, is calculated according to the principle of error propagation; the values are given in Table 3 with the results of the consistency test.

Calorimeter

The heat of mixing was determined with a Picker flow calorimeter [5,9]. The calorimeter was operated 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. Measurements were taken when the signal from the ΔT detector was indicating steady-state conditions.

Densimeter

Densities of pure liquids and their mixtures were determined with two vibrating U-tube instruments (Paar, DMA 602/60, A). Mixtures of two components were prepared gravimetrically using a scale with an error of ±0.2 mg. The density of a pure liquid was determined (see Table 4) after the

TABLE 3

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 n-alkanes with alkylbenzenes; real gas phase behavior calculated with the virial equation of state [a]. The degree of Legendre-polynomials is 3.

Binary system	T (K)	exp pts. n	Est. exp. uncertainty		SIG(Dp) (kPa)	AA(Dy)
			δp (kPa)	δy		
C_8H_{10}–C_9H_{20}	333.15	19	0.03	0.0055	0.020	0.0037
	348.15	16	0.04	0.0037	0.012	0.0011
	363.15	16	0.05	0.0027	0.013	0.0012
C_9H_{20}–C_9H_{12}	353.15	14	0.03	0.0035	0.006	0.0016
	363.15	16	0.03	0.0028	0.006	0.0003
C_8H_{18}–C_9H_{12}	343.15	14	0.02	0.0011	0.014	0.0010 [b]

[a] Second virial coefficients according to Hayden–O'Connell [10].

[b] Gas phase: ideal.

instrument had been calibrated by the reference substances, i.e. distilled water and n-nonane (product Fluka AG (CH), purity > 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 reduced inaccuracies caused by temperature fluctuations in the circulating thermostat liquid.

Pure substances

The alkanes and ethylbenzene were obtained from Fluka AG (CH) in high purity (puriss. p.a., > 99% GC). Propylbenzene was purchased from Merck (F.R.G.) as pro analysi grade (purity > 99% GC). The substances were further purified according to recommendations of Riddick et al. [11].

The n-alkanes were washed several times with concentrated sulfuric acid, treated afterwards with dilute potassium and fractionally distilled in an efficient spinning band column. Ethylbenzene and propylbenzene were fractionally distilled in a column packed with 1 m of 2 mm glass helices. The substances were dried with 4 Å molecular sieves.

The purity of the products was checked by gas chromatography. Purification was continued until trace impurities were no longer detectable. All substances were stored under a nitrogen atmosphere and protected from light. Table 4 compares characteristic properties of the substances, viz. the density, the refractive index and the normal boiling point, with published values.

TABLE 4

Properties of pure liquids: density (d), refractive index (n_D) and normal boiling point (NBP) at 101.325 kPa determined in this work (a), compared with published data

Substance	T (K)	d (g cm^{-3})	Ref.	n_D	Ref.	NBP (K)	Ref.
C_7H_{16}	293.15	0.68360	a	1.3878	a	371.464	a
		0.68376	11	1.38764	11	371.576	12
						371.44	13
C_8H_{18}	298.15	0.69877	a	1.3945	a	398.734	a
		0.69882	14	1.39505	11	398.815	11
C_9H_{20}	293.15	0.71780	15	1.4050	a	423.898	a *
		0.71763	11	1.40542	11	423.948	11
						424.0	16
C_8H_{10}	298.15	0.86252	a	1.4931	a	409.350	a
		0.86264	11	1.49320	11	409.335	12
C_9H_{12}	293.15	0.86197	a	1.4917	a	(433.07)	a *
		0.8620	16	1.4920	16	432.367	17

* Extrapolated.

TABLE 5

Parameters of the Antoine equation* 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(a) and of the literature, where $\mathrm{D(AEQ)} = [\int(\mathrm{AEQ}_1 - \mathrm{AEQ}_2)^2 \mathrm{d}t]^{0.5}/(T_{max} - T_{min})$

Compound	Ref.	$T_{min} - T_{max}$ (K)	A	B	C	SIG(Dp) (kPA)	D(AEQ) (%)
C_8H_{18}	a	295–402	13.9592	3131.04	63.537	0.04	–
	12	326–400	13.9160	3112.53	64.05	–	0.03
	18	287–399	13.9452	3128.75	63.295	–	0.05
C_9H_{20}	a	322–413	14.0832	3372.82	67.547	0.01	–
	17	343–425	13.9595	3293.75	71.342	–	0.02
C_8H_{10}	a	320–400	13.9346	3232.68	62.358	0.01	–
	12	329–410	14.0030	3277.83	60.059	–	0.02
	11	–	14.0045	3279.40	59.944	–	0.03
C_9H_{12}	a	340–391	12.9827	2825.68	95.248	0.03	–
	17	348–433	13.9972	3437.71	65.827	–	0.07

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

TABLE 6

T, p, x, y data and relative volatilities, α_{12}, for coexisting vapor and liquid phases of binary mixtures of n-alkanes with alkylbenzenes

No.	p (kPa)	x_1	y_1	α_{12}	No.	p (kPa)	x_1	y_1	α_{12}
Ethylbenzene–n-nonane, $T = 333.15$ K									
1	4.01	0.0000	0.0000		11	6.53	0.6130	0.7379	1.78
2	4.30	0.0506	0.1175	2.50	12	6.58	0.6168	0.7414	1.78
3	4.63	0.1142	0.2311	2.33	13	6.73	0.6765	0.7816	1.71
4	5.09	0.2135	0.3684	2.15	14	6.88	0.7359	0.8190	1.62
5	5.55	0.3216	0.5010	2.12	15	7.01	0.7900	0.8547	1.56
6	5.89	0.3901	0.5716	2.09	16	7.13	0.8444	0.8896	1.48
7	6.14	0.4728	0.6408	1.99	17	7.22	0.8912	0.9209	1.42
8	6.33	0.5356	0.6830	1.87	18	7.29	0.9263	0.9450	1.37
9	6.33	0.5480	0.6933	1.86	19	7.33	0.9512	0.9629	1.33
10	6.46	0.5777	0.7147	1.83	20	7.37	0.9744	0.9796	1.26
					21	7.40	1.0000	1.0000	
$T = 348.15$ K									
1	7.85	0.0000	0.0000		10	12.61	0.6676	0.7658	1.63
2	8.98	0.1194	0.2222	2.11	11	12.94	0.7360	0.8134	1.56
3	9.52	0.1889	0.3238	2.06	12	12.92	0.7373	0.8139	1.56
4	10.10	0.2634	0.4166	2.00	13	13.19	0.8000	0.8557	1.48
5	10.66	0.3381	0.4993	1.95	14	13.38	0.8573	0.8950	1.42
6	11.14	0.4090	0.5674	1.90	15	13.59	0.9175	0.9373	1.34
7	11.57	0.4795	0.6252	1.81	16	13.67	0.9437	0.9564	1.31
8	12.00	0.5498	0.6825	1.76	17	13.78	0.9799	0.9840	1.26
9	12.34	0.6168	0.7306	1.68	18	13.84	1.0000	1.0000	
$T = 363.150$ K									
1	14.49	0.0000	0.0000		10	21.76	0.6159	0.7205	1.61
2	15.21	0.0453	0.0875	2.02	11	22.29	0.6792	0.7674	1.56
3	16.09	0.1053	0.1885	1.97	12	22.78	0.7447	0.8130	1.49
4	17.12	0.1809	0.2975	1.92	13	23.21	0.8057	0.8559	1.43
5	18.25	0.2692	0.4092	1.88	14	23.56	0.8630	0.8965	1.38
6	19.04	0.3399	0.4847	1.83	15	23.84	0.9142	0.9335	1.32
7	19.85	0.4156	0.5571	1.77	16	24.05	0.9532	0.9630	1.28
8	20.51	0.4818	0.6150	1.72	17	24.18	0.9784	0.9817	1.18
9	21.16	0.5495	0.6696	1.66	18	24.29	1.0000	1.0000	
n-Nonane–n-propylbenzene, $T = 353.15$ K									
1	7.56	0.0000	0.0000		9	9.08	0.4473	0.5079	1.28
2	7.68	0.0255	0.0376	1.49	10	9.27	0.5561	0.6027	1.21
3	7.89	0.0640	0.0981	1.59	11	9.39	0.6465	0.6799	1.16
4	8.11	0.1151	0.1678	1.55	12	9.51	0.7452	0.7654	1.12
5	8.32	0.1704	0.2357	1.50	13	9.58	0.8373	0.8458	1.07
6	8.55	0.2390	0.3096	1.43	14	9.62	0.9236	0.9261	1.04
7	8.75	0.3131	0.3839	1.37	15	9.64	0.9716	0.9721	1.02
8	8.92	0.3805	0.4490	1.33	16	9.63	1.0000	1.0000	
$T = 363.15$ K									
1	11.44	0.0000	0.0000		10	13.57	0.4476	0.5083	1.28
2	11.62	0.0263	0.0416	1.61	11	13.77	0.5149	0.5680	1.24

TABLE 6 (continued)

No.	p (kPa)	x_1	y_1	α_{12}	No.	p (kPa)	x_1	y_1	α_{12}
3	11.93	0.0708	0.1057	1.55	12	13.93	0.5817	0.6255	1.20
4	12.22	0.1186	0.1689	1.51	13	14.11	0.6684	0.7002	1.16
5	12.51	0.1737	0.2357	1.47	14	14.23	0.7430	0.7646	1.12
6	12.81	0.2382	0.3066	1.41	15	14.34	0.8292	0.8405	1.09
7	13.05	0.2984	0.3680	1.37	16	14.41	0.9050	0.9096	1.06
8	13.27	0.3594	0.4268	1.33	17	14.45	0.9601	0.9615	1.04
9	13.39	0.3890	0.4556	1.31	18	14.46	1.0000	1.0000	
n – Octane–n-propylbenzene, T = 343.15 K									
1	4.98	0.0000	0.0000		8	10.18	0.3978	0.6895	3.36
2	5.53	0.0330	0.1264	4.24	9	11.03	0.4757	0.7440	3.20
3	6.52	0.0964	0.3054	4.12	10	12.31	0.6120	0.8235	2.96
4	7.51	0.1691	0.4432	3.91	11	13.31	0.7209	0.8782	2.79
5	8.44	0.2399	0.5444	3.79	12	14.30	0.8255	0.9253	2.62
6	9.03	0.2960	0.6007	3.58	13	15.25	0.9275	0.9696	2.49
7	9.15	0.3046	0.6094	3.56	14	15.92	1.0000	1.0000	

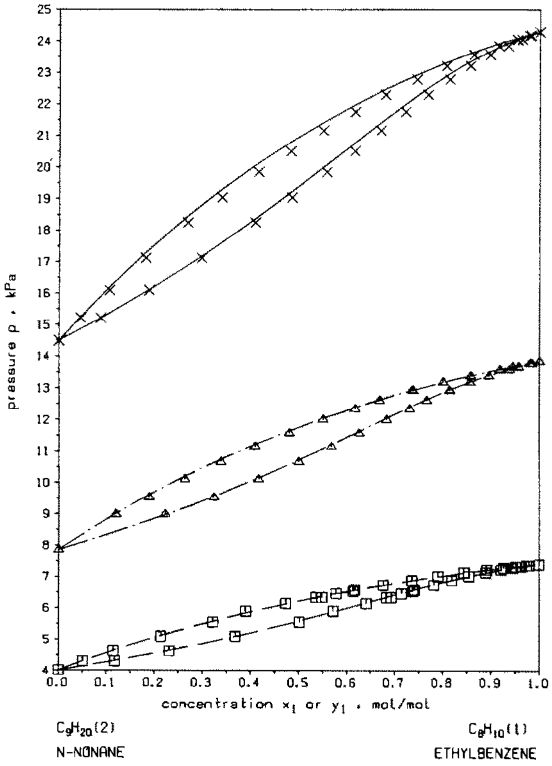

Fig. 1. Experimental and calculated VLE for the system C_8H_{10}–C_9H_{20}. Points: experimental $p-x$, y data, $T = 333.15$ K (□), $T = 348.15$ K (△) and $T = 363.15$ K (×); lines: Unifac prediction.

TABLE 7

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)
C_8H_{10}–C_9H_{20}	333.15	0.02	0.003	0.004
	348.15	0.05	0.004	0.004
	363.15	0.17	0.008	0.005
C_9H_{20}–C_9H_{12}	353.15	0.05	0.006	0.005
	363.15	0.14	0.010	0.005
C_8H_{18}–C_9H_{12}	343.15	0.05	0.005	0.002

[a] Gas phase nonidealities neglected.

TABLE 8

Experimental h^E–x data for mixtures of n-alkanes with alkylbenzenes

No.	x_1	h^E (J mol^{-1})	No.	x_1	h^E (J mol^{-1})	No.	x_1	h^E (J mol^{-1})
n-Heptane–ethylbenzene, T = 288.15 K								
1	0.1639	287.9	8	0.4104	510.1	14	0.6380	495.0
2	0.1974	335.4	9	0.4459	521.3	15	0.6770	471.4
3	0.2323	380.5	10	0.4829	528.0	16	0.7161	439.7
4	0.2729	416.2	11	0.5228	527.5	17	0.7569	402.9
5	0.3020	447.2	12	0.5596	522.4	18	0.7963	358.2
6	0.3380	473.8	13	0.5964	511.2	19	0.8323	307.5
7	0.3740	494.9						
T = 308.15 K								
1	0.1359	264.8	8	0.3740	502.0	15	0.6380	485.7
2	0.1639	313.0	9	0.4104	515.5	16	0.6770	459.2
3	0.1974	358.5	10	0.4459	524.5	17	0.7161	426.4
4	0.2323	398.5	11	0.4829	528.0	18	0.7569	387.2
5	0.2729	431.5	12	0.5228	526.4	19	0.7963	342.8
6	0.3020	460.0	13	0.5596	517.7	20	0.8323	292.5
7	0.3380	483.4	14	0.5964	504.5			
n-Octane–n-propylbenzene, T = 298.15 K								
1	0.1650	262.2	7	0.3756	408.4	13	0.6010	411.6
2	0.1992	297.9	8	0.4121	419.1	14	0.6402	396.8
3	0.2336	327.1	9	0.4490	425.6	15	0.6798	375.6
4	0.2685	353.0	10	0.4863	429.5	16	0.7199	348.1
5	0.3038	375.6	11	0.5241	428.0	17	0.7604	315.3
6	0.3395	394.2	12	0.5623	421.9	18	0.8015	275.8
T = 308.15 K								
1	0.1650	259.0	7	0.3756	406.0	13	0.6010	406.6
2	0.1992	294.0	8	0.4121	417.2	14	0.6402	389.8
3	0.2336	326.6	9	0.4490	425.2	15	0.6798	367.9
4	0.2685	353.8	10	0.4863	430.5	16	0.7199	340.2
5	0.3038	375.4	11	0.5241	426.6	17	0.7604	306.1
6	0.3395	391.8	12	0.5623	418.9	18	0.8015	265.3

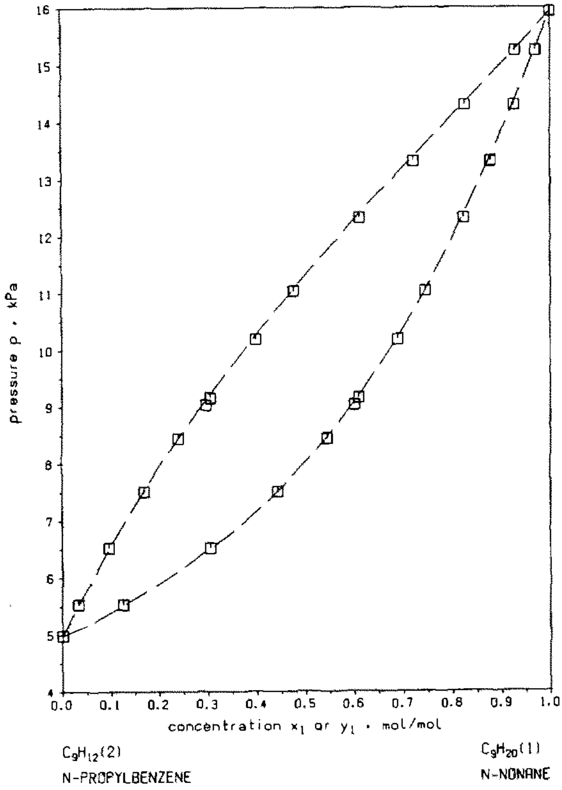

Fig. 2. Experimental and calculated VLE for the system $C_8H_{18}-C_9H_{12}$. Points: experimental $p - x$, y data, $T = 343.15$ K (⊞); lines: Unifac prediction.

EXPERIMENTAL RESULTS

Vapor pressures of pure liquids

Measurement of the vapor 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, the comparison between measured and calculated points provides an indication of the scattering and the reproducibility of the data, especially if the vapor pressures were measured twice, i.e. once with increasing and once with decreasing temperature.

(3) The pure-component vapor pressures must be known for reduction of binary data.

Table 5 lists, for all liquids investigated in the Stage cell, coefficients of the Antoine equation and the integrated deviation in relative pressure between two Antoine equations.

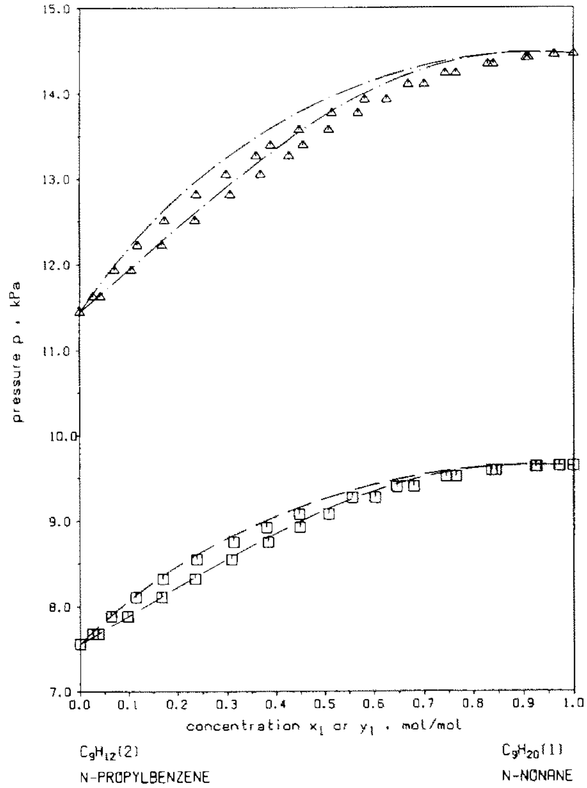

Fig. 3. Experimental and calculated VLE for the system C_9H_{20}–C_9H_{12}. Points: experimental $p-x$, y data, $T = 353.15$ K (□), and $T = 363.15$ K (△): lines. Unifac prediction.

Vapor–liquid equilibria

Temperature, pressure and the mole fractions of liquid and vapor were measured in the equilibrium apparatus. Table 6 presents all experimental data as well as the relative volatility, α_{12}. Figures 1–3 show experimental bubble and dewpoints. For comparison, they also show the isotherms

TABLE 9

Coefficients of eqn. (1), standard deviations and maximum deviations for the h^E measurements

Binary system	T (K)	A_1	A_2	A_3	SIG(Dh^E) (J mol^{-1})	Dh^E_{max} (J mol^{-1})
C_8H_{10}–C_7H_{16}	288.15	2115.9	63.8	120.6	1.97	3.71
	308.15	2100.4	−107.4	179.1	2.13	4.35
C_8H_{18}–C_9H_{12}	298.15	1714.9	−80.2	243.8	2.09	3.47
	308.15	1708.3	−121.2	152.2	2.38	3.86

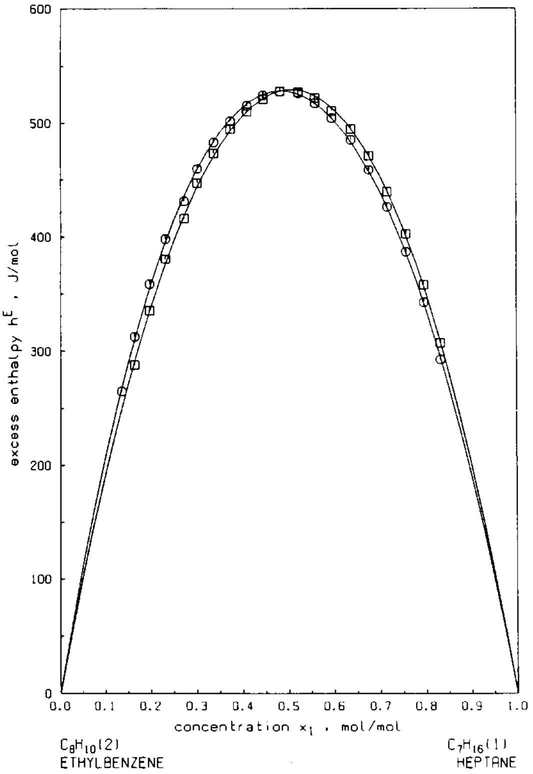

Fig. 4. Experimental and calculated h^E data. Points: Experimental h^E for C_7H_{16}–C_8H_{10} at $T = 288.15$ K (□) and $T = 308.15$ K (⦶); lines represent the calculations of Redlich–Kister polynomials with parameters given in Table 9.

calculated from the Unifac model [1] without adjusting parameters to the new data (see also Table 7).

Excess enthalpies

Results of the caloric experiments are shown in Table 8 and in Figs. 4 and 5.

Excess volumes

Experimental results of v^E for all systems are presented in Table 10 and Fig. 6.

DATA REDUCTION

Consistency test of VLE data

With the redundant information of T, p, x and y data the consistency of

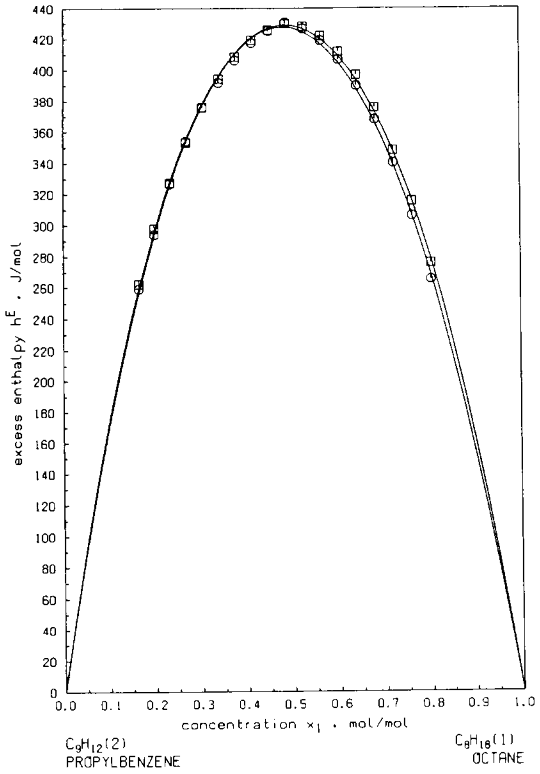

Fig. 5. Experimental and calculated h^E data. Points: Experimental h^E for C_8H_{18}–C_9H_{12} at $T = 298.15$ K (◫) and $T = 308.15$ K (○); lines represent the calculations of Redlich–Kister polynomials with parameters given in Table 9.

the experimental VLE results can be checked according to the Gibbs–Duhem equation. In the present work the test suggested by Van Ness [19] in the version of Fredenslund [1] is applied to the data. However, the test is only applicable if vapor-phase properties can be reliably predicted.

Here the truncated virial equation of state was used with second virial coefficients from Hayden and O'Connell [10]. The liquid molar volume is calculated by the correlation of Hankinson et al. [20]. The Poynting correction is calculated assuming v^L_{0i} to be independent of pressure.

The absolute average deviation AA(Dy) and the Dy vs. x plot are indications of the consistency and, probably the accuracy of the data (see Table 3). As the deviations AA(Dy) of the isotherms are less than 0.01 mol mol^{-1} (the criterion for consistency proposed by Fredenslund [1]) and less than the experimental uncertainties, the T, p, x, y sets can be considered consistent.

Models for the excess Gibbs energy

(1) Based on the experimental data and additional information about the thermophysical properties, it is possible to determine the activity coefficients

TABLE 10

Experimental v^E-x data for mixtures of n-alkanes with alkylbenzenes

No.	x_1	v^E (cm^3 mol^{-1})	No.	x_1	v^E (cm^3 mol^{-1})	No.	x_1	v^E (cm^3 mol^{-1})
n-Heptane–ethylbenzene, $T = 298.15$ K								
1	0.0622	0.0084	5	0.3774	0.0215	9	0.6579	0.0369
2	0.1534	0.0152	6	0.5009	0.0322	10	0.7073	0.0352
3	0.2008	0.0194	7	0.5660	0.0302	11	0.7500	0.0331
4	0.2537	0.0190	8	0.6096	0.0340	12	0.8053	0.0327
Ethylbenzene–n-nonane, $T = 293.15$ K								
1	0.0263	0.0267	5	0.4866	0.2905	8	0.8958	0.1133
2	0.1689	0.1612	6	0.6668	0.2744	9	0.9467	0.0663
3	0.2010	0.1792	7	0.8084	0.1926	10	0.9731	0.0385
4	0.3505	0.2437						
n-Octane–n-propylbenzene, $T = 293.15$ K								
1	0.0056	0.0003	5	0.1745	0.0506	9	0.7776	0.0420
2	0.0169	0.0055	6	0.3499	0.0626	10	0.9126	0.0196
3	0.0390	0.0148	7	0.4877	0.0666	11	0.9460	0.0101
4	0.0957	0.0287	8	0.6403	0.0555	12	0.9745	0.0096
$T = 298.15$ K								
1	0.0602	0.0178	5	0.4004	0.0690	9	0.7547	0.0578
2	0.1537	0.0386	6	0.5677	0.0745	10	0.7996	0.0502
3	0.2879	0.0656	7	0.6557	0.0652	11	0.8528	0.0391
4	0.3509	0.0691	8	0.7034	0.0614			
n-Nonane–n-propylbenzene, $T = 293.15$ K								
1	0.0503	0.0403	7	0.2564	0.1513	12	0.6779	0.1724
2	0.1042	0.0780	8	0.3435	0.1806	13	0.7246	0.1324
3	0.1588	0.1101	9	0.4734	0.1983	14	0.7248	0.1125
4	0.1588	0.1102	10	0.5621	0.1927	15	0.7248	0.1126
5	0.1824	0.1248	11	0.5621	0.1972	16	0.8457	0.0735
6	0.2564	0.1471						

TABLE 11

Coefficients of eqn. (1), standard deviations and maximum deviations for the v^E measurements

Component	T (K)	A_1	A_2	A_3	SIG(Dv^E) (cm^3 mol^{-1})	Dv^E_{max} (cm^3 mol^{-1})
C_7H_{16}–C_8H_{10}	298.15	0.1163	0.0717	0.1213	0.0019	0.0031
C_9H_{20}–C_8H_{10}	293.15	1.1489	−0.1426	0.0829	0.0071	0.0098
C_8H_{18}–C_9H_{12}	293.15	0.2760	−0.0086	−0.0006	0.0053	0.0099
	298.15	0.2976	0.0026	0.0243	0.0022	0.0039
C_9H_{20}–C_9H_{12}	293.15	0.7747	−0.2000	−0.1785	0.0111	0.0237

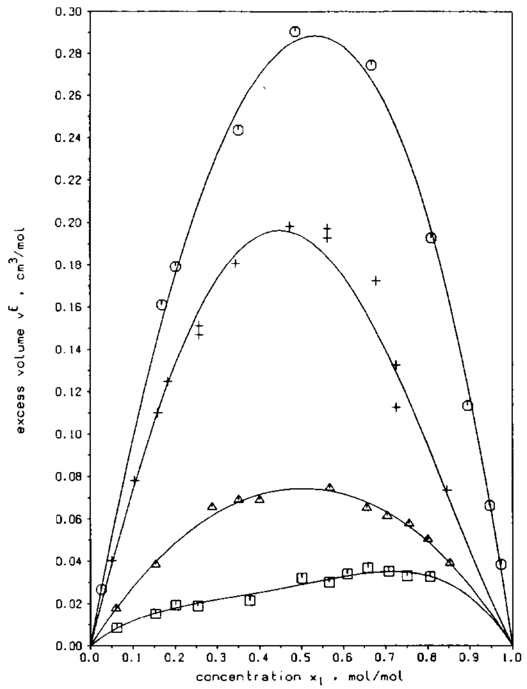

Fig. 6. Experimental and calculated v^E data. Points: Experimental v^E for C_7H_{16} (1)–C_8H_{10} (2) at $T = 298.15$ K (□), C_8H_{10} (1)–C_9H_{20} (2) at $T = 293.15$ K (⦶), C_8H_{18} (1)–C_9H_{12} (2) at $T = 298.15$ K (△) and C_9H_{20} (1)–C_9H_{12} (2) at $T = 293.15$ K (+); lines represent the calculations of Redlich–Kister polynomials with parameters given in Table 11.

for each experimental point. The experimental data sets were used to fit binary parameters for five "popular" g^E models [16] with the method of Prausnitz and Anderson [21]. Table 12 gives the results of the parameter estimation for the model, which represents the data best. Figure 7 presents the results for the systems C_8H_{10}–C_9H_{20} and C_9H_{20}–C_9H_{12} showing the g^E points calculated from the experimental data and curves from the Uniquac model.

(2) Reliable experimental VLE data also serve to extend and improve group contribution methods and their parameter tables. As it is shown in Table 7 and Figs. 1–3, Unifac predictions using group interactions reported in ref. 1 agree satisfactorily with our new data.

Redlich-Kister polynomial for h^E

Experimental h^E–x data are usually correlated by a polynominal proposed by Redlich and Kister:

$$h^E = x_1 x_2 \Sigma (x_1 - x_2)^{k-1} A_k \qquad k = 1, \ldots, m \tag{1}$$

TABLE 12

Results of the parameter estimation using the algorithm of Prausnitz et al. [21]

System (1): ethylbenzene–n-nonane			
Temperature (K)	333.15	348.15	363.15
Equation [16]	Uniquac	Wilson	Wilson
Parameter [a] X_{12}	257.48	372.73	552.65
X_{21}	−70.69	772.25	416.34
$\gamma_{\infty 1}$	1.284	1.262	1.238
$\gamma_{\infty 2}$	1.521	1.442	1.355
SIG(Dp) (kPa)	0.021	0.014	0.018
SIG(Dy)	0.0031	0.0012	0.0010
System (2): n-nonane–n-propylbenzene			
Temperature (K)	353.15	363.15	
Equation [16]	Van Laar	Wilson	
Parameter [a] X_{12}	0.3034	325.94	
X_{21}	0.2270	461.86	
$\gamma_{\infty 1}$	1.355	1.295	
$\gamma_{\infty 2}$	1.255	1.235	
SIG(Dp) (kPa)	0.009	0.007	
SIG(Dy)	0.0019	0.0004	
System (3): n-octane–n-propylbenzene [b]			
Temperature (K)	343.15		
Equation [12]	Uniquac		
Parameter [a] X_{12}	106.95		
X_{21}	26.40		
$\gamma_{\infty 1}$	1.389		
$\gamma_{\infty 2}$	1.319		
SIG(Dp) (kPa)	0.020		
SIG(Dy)	0.0013		

[a] Uniquac, NRTL and Wilson parameters in J mol^{-1} (third NRTL, parameter $\alpha = 0.3$).
[b] Gas phase ideal.

The degree $m - 1$ and the number of adjustable coefficients m depend on the complexity of the mixture. Table 9 lists the coefficients of the isotherms for the binary systems.

Figure 8 shows, for the system C_7H_{16}–C_8H_{10} at $T = 308.15$ K, curves for h^E, partial molar excess enthalpies h_i^E, and $h^E/(x_1x_2)$ 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 (eqn. 1). Table 11 gives coefficients of the correlation as well as standard and maximum deviations (see also Fig. 6).

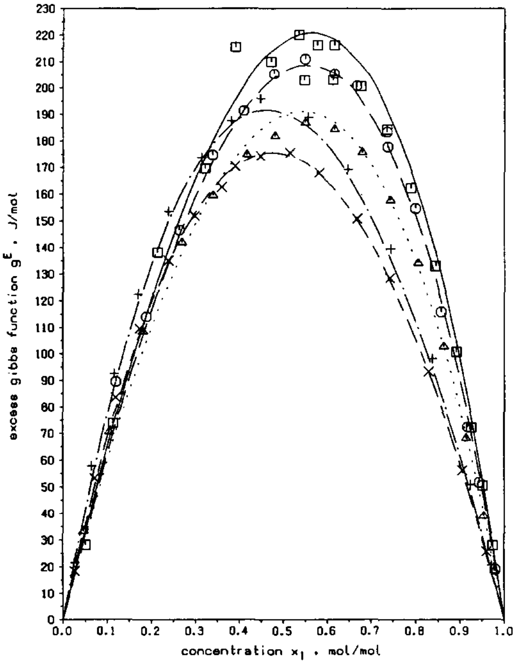

Fig. 7. Experimental and calculated g^E vs. composition. Points: Reduced experimental data for the system C_8H_{10} (1)–C_9H_{20} (2) at $T = 333.15$ K (◫), $T = 348.15$ K (⦶) and $T = 363.15$ K (△), and for the system C_9H_{20} (1)–C_9H_{12} (2) at $T = 353.15$ K (+) and T = 363.15 K (×); lines: Calculated values with the Uniquac equation using parameters fitted to the data set.

RESULTS

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.

In this study new experimental data on VLE, h^E and v^E of binary mixtures are presented to fill the gaps in the data tables and to provide a basis for theoretical investigations. The experimental VLE results verify that the Unifac parameters for the methyl group (CH_2) and the aromatic group (ACH) allow predictions of reasonable accuracy.

ACKNOWLEDGMENTS

The authors wish to thank Prof. H.V. Kehiaian for helpful discussions and advice. The great amount of experimental work could not have been accomplished without the cooperation of Mrs. C. Eichenauer.

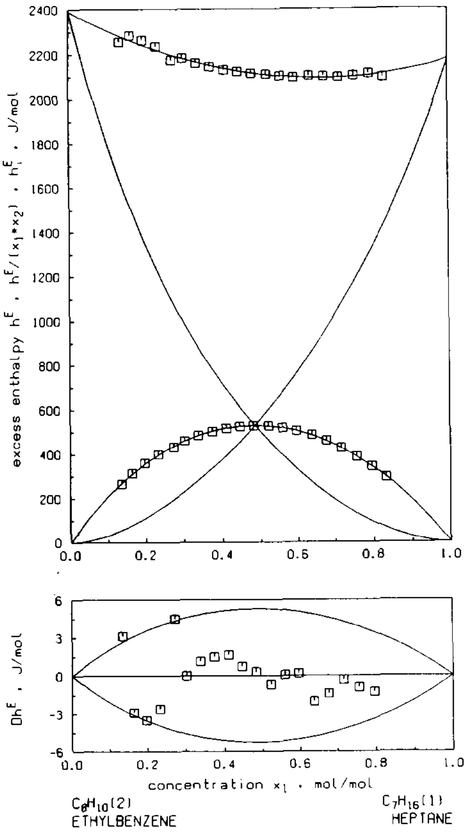

Fig. 8. h^E, $h^E/(x_1x_2)$ and h_1^E, h_2^E vs. composition for the system C_7H_{16}–C_8H_{10} as well as the deviations Dh^E between experimental and calculated points. Points: Experimental data at $T = 308.15$ K; lines: Calculated by Redlich Kister equation. The lens shaped curve in the Dh^E plot indicates 1% deviation.

LIST OF SYMBOLS

A, B, C	Antoine constants
A_k	kth coefficient of polynomial
AA(Dz)	absolute average deviation, $= (1/n)\sum_{i}^{n} \lvert z - z^+ \rvert_i$
d	density (g cm^{-3})
Dz	deviation, $= z - z^+$
g	molar Gibbs energy (J mol^{-1})
h	molar enthalpy (J mol^{-1})
h_i	partial molar enthalpy (J mol^{-1})
m	number of adjustable parameters
n	number of experimental points
NBP	normal boiling temperature (K)

n_D	refractive index
p	pressure (hPa, kPa)
RMS(Dz)	root mean square deviation, $= [1/n)\sum_{i}^{n}(z - z^{+})_i^2]^{0.5}$
s	molar entropy (J mol^{-1} K^{-1})
SIG(Dz)	standard deviation, $= \{[1/(n - m)]\sum_{i}^{n}(z - z^{+})_i^2\}^{0.5}$
T	temperature (K)
t	degree of polynomial
v	molar volume (cm^3 mol^{-1})
X	parameter of g^E model
x	composition of liquid (mol mol^{-1})
y	composition of vapor (mol mol^{-1})
z	measurable quantity

Greek letters

α	relative volatility
α_{12}	$= (y_1/x_1)/(y_2/x_2)$
δ	experimental uncertainty
ψ	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

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