

## VAPOR - LIQUID EQUILIBRIUM OF SYSTEMS CONTAINING PERFLUOROMETHYL-CYCLOHEXANE AND HYDROCARBONS

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### ABSTRACT

Vapor - liquid equilibrium data for the binary systems: Perfluoromethylcyclohexane + n-Hexane and Perfluoromethylcyclohexane + 1-Hexene were determined at 93.3 KPa and 328.15 K.

The vapor pressure for the pure components were also measured to calculate the Antoine constants.

The data were correlated by using the Van-Laar, Margules, Wilson, NRTL and UNIQUAC equations.

UNIFAC group-contribution parameters between CH<sub>2</sub> and CF<sub>2</sub>, and CH<sub>2</sub>=CH and CF<sub>2</sub> were also calculated.

### INTRODUCTION

Following our experimental determination of binary solubilities (Bernardo-Gil and Soares, 1987, 1988) and liquid - liquid equilibria for some multicomponent perfluorocarbon + hydrocarbon systems (Bernardo-Gil and Soares, 1986b, 1989, 1990), this paper reports the results of measurements on vapor - liquid equilibrium for binary systems containing perfluoromethylcyclohexane + n-hexane or + 1-hexene at 93.3 KPa and 328.15 K. The temperature of 328.15 K was selected for the isothermal determination because it is close to the azeotropic boiling points at 93.3 KPa.

The thermodynamic consistency of the data was tested by using the method described by Fredenslund et al. (1977). All the data are consistent.

A Nelder - Mead technique was used to reduce the data, minimizing an objective function based on the total pressure, providing the relevant Van-Laar, Margules, Wilson, NRTL and UNIQUAC parameters (Bernardo-Gil and Soares, 1986a).

The same technique was used to calculate the UNIFAC parameters for the contributions CH<sub>2</sub>/CF<sub>2</sub>, CF<sub>2</sub>/CH<sub>2</sub>, CH<sub>2</sub>=CH/CF<sub>2</sub> and CF<sub>2</sub>/CH<sub>2</sub>=CH.

### EXPERIMENTAL

Perfluoromethylcyclohexane (Aldrich-Europe, 99 %, GC, IR), n-hexane (Merck, p.a., 99 %, GC) and 1-hexene (Fluka, 99 %) were used as supplied.

The experimental determinations were made in a miniature still (Figure 1), requiring a liquid charge of approximately 25 ml.

The compositions of both phases were analysed by using a gas chromatograph equipped with a flame ionization detector and an integrator. Calibration analysis were carried out to convert the peak-area ratios to actual mole fractions of both components in the mixtures.

The main feature of the still is the direct sampling of the vapor phase, prior to condensation, into the gas chromatograph, thus overcoming the difficulty of sampling a partially miscible condensate. A glass capillary line ( $S_v$ ) was let in the vapor line from the top of the still to the cold finger condenser (C). The condensate returns to the bottom of the still by a capillary line (D). A magnetic stirrer (S) in the liquid phase enables perfect mixing of the returned condensate, insuring the uniformity of composition of the liquid phase. The level of liquid was maintained slightly above the end of the thermometer well ( $T_L$ ). The heating chamber (B) was maintained at a temperature of  $0.5^\circ\text{C}$  above the boiling point of the solution, thus eliminating all partial condensation without vapor phase superheating. Samples from liquid phase were withdrawn from the liquid sampling port ( $S_L$ ) with a pre-heated chromatographic syringe and injected into the chromatograph.

Although the period required for attainment of the steady state was about 10-15 minutes, the still was allowed to run for 30 minutes after which samples of liquid and vapor were taken alternately and analysed. Standard deviations of 0.1 % to 0.5 % on mole compositions were obtained.

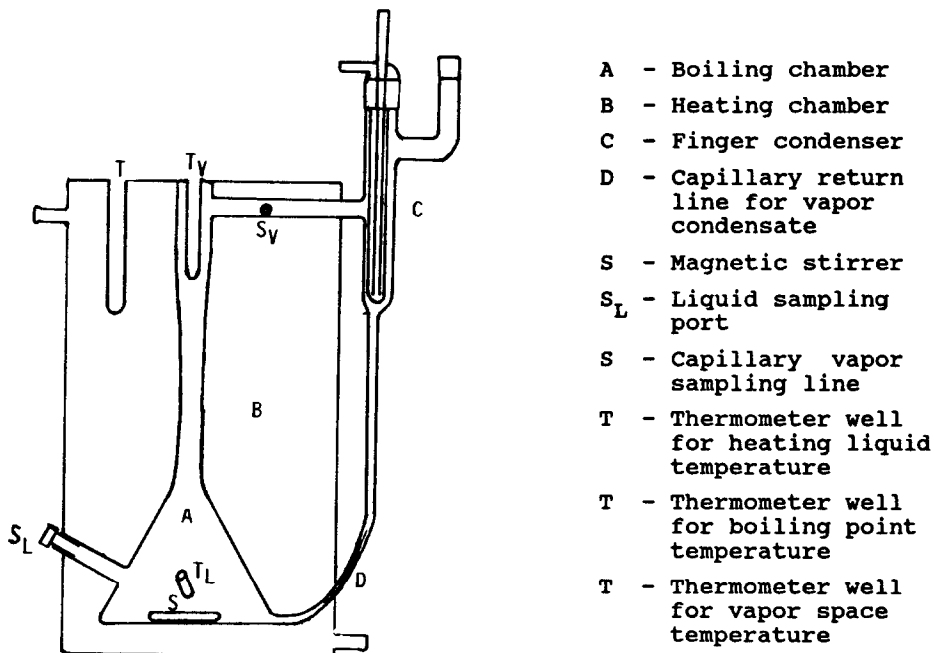


Fig. 1. Miniature equilibrium still

The condenser was connected to the vacuum pump via a cold trap. A pressure controller capable of controlling the pressure to within  $\pm 0.1$  mm Hg and a surge tank were used to maintaining a constant pressure. The pressure in the still was measured by means a vertical mercury U-tube manometer and a cathetometer to within  $\pm 0.1$  mm Hg.

Equilibrium temperatures were measured by using calibrated PT100 resistances connected to a digital thermometer, and could be measured to  $\pm 0.05$  °C or better.

## RESULTS AND DATA ANALYSIS

The experimental vapor - liquid equilibrium data for perfluoromethylcyclohexane / n-hexane and perfluoromethylcyclohexane / 1-hexene at 328.15 K and 93.3 KPa are presented in tables 1 and 2.

The data were reduced by means of a Nelder - Mead technique to minimize the following objective function (Bernardo-Gil and Soares, 1982):

$$F = \sum_{i=1}^N (P_i^{\text{cal}} - P_i^{\text{exp}})^2 \quad (1)$$

where N is the number of data points.

The Van-Laar, Margules (Margules, 1895), Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) equations were used to describe the liquid phase activity coefficients. The numerical values of binary parameters for the systems studied are presented in Table 3.

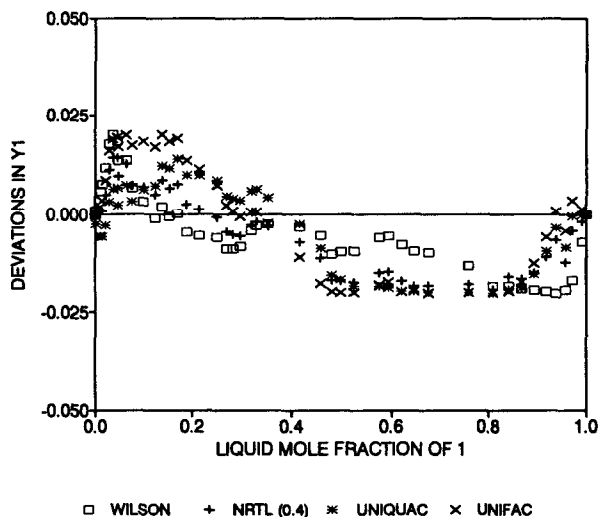


Fig. 2. Deviations between calculated and experimental vapor - liquid mole fractions of component 1 for perfluoromethylcyclohexane (1) / n-hexane (2) at 328.15 K.

TABLE 1

Experimental vapor - liquid equilibrium data for perfluoromethyl-cyclohexane (1) + n-hexane (2)

P = 93.3 KPa			T = 328.15 K		
T (K)	$x_1$	$y_1$	P (KPa)	$x_1$	$y_1$
338.67	0.0024	0.0165	64.6	0.0005	0.0032
337.78	0.0068	0.0443	65.3	0.0026	0.0180
336.03	0.0172	0.0993	68.4	0.0116	0.0684
335.32	0.0222	0.1213	69.7	0.0160	0.0890
333.70	0.0365	0.1726	71.5	0.0224	0.1128
331.01	0.0797	0.2639	73.3	0.0300	0.1350
330.17	0.1080	0.2961	75.1	0.0378	0.1570
329.73	0.1312	0.3141	76.8	0.0468	0.1820
329.54	0.1472	0.3236	77.2	0.0490	0.1921
329.50	0.1515	0.3259	79.7	0.0658	0.2248
329.21	0.1945	0.3428	81.1	0.0762	0.2480
329.20	0.2015	0.3449	83.6	0.0999	0.2800
329.11	0.2240	0.3507	85.2	0.1250	0.3060
329.07	0.2405	0.3543	86.0	0.1392	0.3130
329.01	0.2820	0.3617	86.7	0.1536	0.3240
328.97	0.3078	0.3655	87.3	0.1708	0.3320
328.90	0.3390	0.3699	88.1	0.1892	0.3450
328.87	0.3576	0.3724	88.8	0.2150	0.3550
328.84	0.3930	0.3773	89.3	0.2492	0.3660
328.87	0.4379	0.3841	89.6	0.2690	0.3740
328.93	0.4625	0.3882	89.7	0.2812	0.3770
328.98	0.4955	0.3943	89.9	0.2970	0.3800
329.03	0.5126	0.3829	90.0	0.3188	0.3806
329.11	0.5320	0.3875	90.0	0.3294	0.3814
329.21	0.5535	0.3930	90.1	0.3540	0.3860
329.44	0.5908	0.4042	90.1	0.4176	0.3984
329.96	0.6415	0.4228	89.8	0.4590	0.4080
330.07	0.6576	0.4297	89.7	0.4810	0.4170
330.56	0.6965	0.4490	89.7	0.4990	0.4200
330.63	0.7000	0.4508	89.4	0.5252	0.4250
331.00	0.7240	0.4650	89.0	0.5764	0.4330
331.35	0.7425	0.4772	88.8	0.5946	0.4370
331.59	0.7535	0.4851	88.1	0.6198	0.4460
332.15	0.7775	0.5014	87.4	0.6450	0.4550
332.67	0.7960	0.5202	86.8	0.6740	0.4650
332.90	0.8045	0.5289	83.3	0.7590	0.5060
333.82	0.8316	0.5586	79.7	0.8111	0.5460
334.90	0.8580	0.5932	77.1	0.8440	0.5758
335.38	0.8680	0.6082	74.1	0.8710	0.6108
336.70	0.8920	0.6486	70.8	0.8960	0.6492
337.37	0.9035	0.6715	67.2	0.9200	0.6940
338.60	0.9210	0.7102	63.6	0.9400	0.7408
339.73	0.9255	0.7473	59.7	0.9590	0.8080
340.82	0.9480	0.7837	56.5	0.9730	0.8560
341.71	0.9572	0.8135	51.2	0.9930	0.9570
342.90	0.9685	0.8544			
343.27	0.9718	0.8671			
343.51	0.9740	0.8759			
345.60	0.9905	0.9502			
346.07	0.9937	0.9663			

In figures 2-5 are shown the deviations between the calculated values of  $y$  obtained using the Wilson, the NRTL, the UNIQUAC and the UNIFAC equations and the experimental ones, for the systems studied.

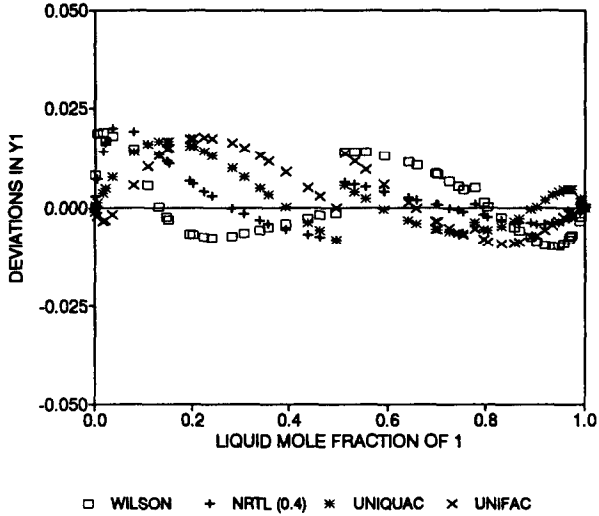


Fig. 3. Deviations between calculated and experimental vapor-liquid mole fractions of component 1 for perfluoromethylcyclohexane (1) / n-hexane (2) at 93.3 KPa.

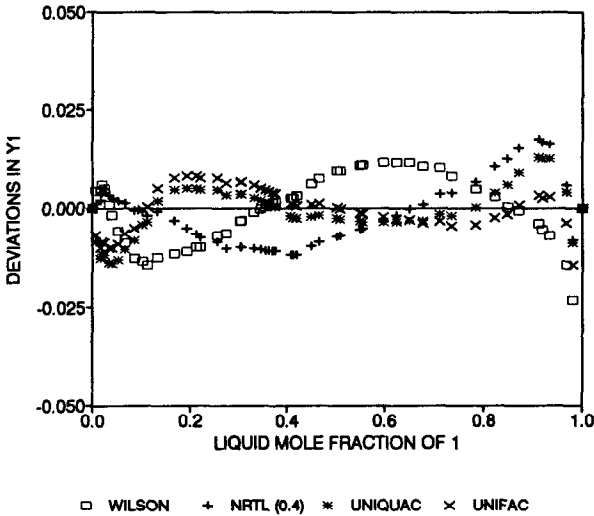


Fig. 4. Deviations between calculated and experimental vapor-liquid mole fractions of component 1 for perfluoromethylcyclohexane (1) / 1-hexene (2) at 328.15 K.

TABLE 2

Experimental vapor - liquid equilibrium data for perfluoromethyl-  
cyclohexane (1) + 1-hexene (2)

P = 93.3 KPa			T = 328.15 K		
T (K)	$x_1$	$y_1$	P (KPa)	$x_1$	$y_1$
334.29	0.0058	0.0337	80.1	0.0082	0.0560
333.16	0.0112	0.0595	83.5	0.0170	0.1019
332.22	0.0183	0.0920	84.4	0.0196	0.1114
331.33	0.0312	0.1390	86.3	0.0258	0.1352
329.69	0.0410	0.1660	88.6	0.0348	0.1658
328.86	0.0673	0.2204	90.0	0.0410	0.1830
327.39	0.0815	0.2395	92.2	0.0528	0.2092
327.00	0.1160	0.2684	94.2	0.0670	0.2322
326.20	0.1355	0.2790	96.2	0.0858	0.2555
325.99	0.1638	0.2904	97.4	0.1029	0.2690
325.80	0.2105	0.3040	97.9	0.1124	0.2760
325.67	0.2572	0.3126	98.8	0.1332	0.2845
325.58	0.2640	0.3143	99.7	0.1680	0.2966
325.42	0.2750	0.3168	100.0	0.1925	0.3030
325.42	0.2795	0.3184	100.4	0.2124	0.3070
325.40	0.2880	0.3200	100.6	0.2205	0.3088
325.40	0.2935	0.3210	100.9	0.2545	0.3130
325.40	0.2995	0.3220	101.0	0.2748	0.3163
325.40	0.3225	0.3245	101.0	0.3040	0.3183
325.40	0.3530	0.3278	101.0	0.3045	0.3183
325.40	0.3735	0.3300	101.0	0.3310	0.3209
325.42	0.3915	0.3315	100.9	0.3448	0.3225
325.51	0.3940	0.3320	100.8	0.3542	0.3236
325.61	0.4270	0.3360	100.8	0.3615	0.3244
325.66	0.4348	0.3362	100.6	0.3700	0.3254
325.67	0.4433	0.3386	100.6	0.3760	0.3261
325.87	0.4990	0.3490	100.3	0.4080	0.3310
325.90	0.5070	0.3500	100.3	0.4125	0.3317
326.21	0.5640	0.3640	100.4	0.4200	0.3326
326.40	0.5892	0.3716	100.1	0.4507	0.3355
327.45	0.6775	0.4060	100.0	0.4655	0.3370
327.64	0.6892	0.4119	99.5	0.5034	0.3434
328.70	0.7420	0.4437	99.4	0.5092	0.3446
329.07	0.7545	0.4527	98.6	0.5495	0.3532
330.70	0.8070	0.4994	98.5	0.5560	0.3549
330.92	0.8125	0.5051	97.4	0.5970	0.3660
332.48	0.8482	0.5485	96.5	0.6225	0.3744
332.72	0.8525	0.5541	95.4	0.6490	0.3841
333.95	0.8740	0.5873	94.1	0.6777	0.3969
334.55	0.8842	0.6049	92.1	0.7118	0.4137
336.24	0.9088	0.6547	90.6	0.7345	0.4285
337.97	0.9288	0.7050	86.5	0.7835	0.4650
339.06	0.9400	0.7380	82.3	0.8240	0.5037
339.66	0.9460	0.7570	79.1	0.8505	0.5364
340.51	0.9530	0.7808	75.9	0.8730	0.5687
341.27	0.9605	0.8083	69.2	0.9130	0.6462
342.48	0.9700	0.8462	68.0	0.9200	0.6640
342.85	0.9730	0.8592	65.1	0.9345	0.7037
344.63	0.9855	0.9175	57.3	0.9690	0.8345
345.80	0.9930	0.9580	54.2	0.9815	0.9050

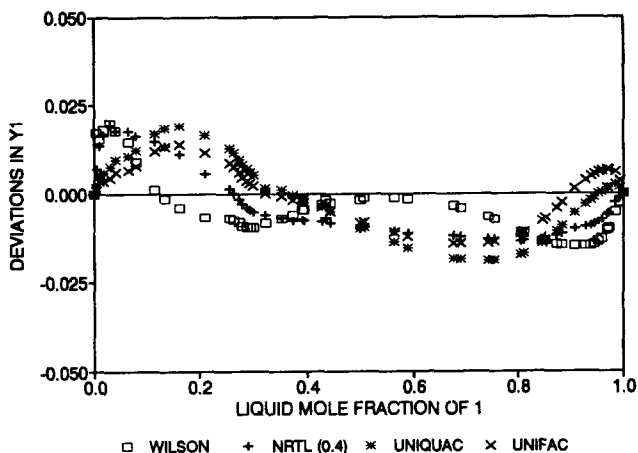


Fig. 5. Deviations between calculated and experimental vapor-liquid mole fractions of component 1 for perfluoromethylcyclohexane (1) / 1-hexene (2) at 93.3 KPa.

TABLE 3  
Model parameters

Equation	$A_{12}$	$A_{21}$	$\alpha_{12}$
<i>Perfluoromethylcyclohexane / n-hexane at 328.15 K</i>			
Van-Laar	2.074	1.593	
Margules	2.038	1.574	
Wilson	845.3	877.7	
NRTL	521.86	1046.8	0.40
UNIQUAC	309.1	-29.20	
<i>Perfluoromethylcyclohexane / n-hexane at 93.3 KPa</i>			
Van-Laar	2.318	1.467	
Margules	2.199	1.417	
Wilson	1163.0	744.3	
NRTL	428.7	1267.5	0.40
UNIQUAC	563.6	308.7	
<i>Perfluoromethylcyclohexane / 1-hexene at 328.15 K</i>			
Van-Laar	2.306	1.396	
Margules	2.184	1.317	
Wilson	1085.5	746.5	
NRTL	316.7	1387.1	0.40
UNIQUAC	188.0	79.54	
<i>Perfluoromethylcyclohexane / 1-hexene at 93.3 KPa</i>			
Van-Laar	2.407	1.435	
Margules	2.258	1.377	
Wilson	1197.8	749.8	
NRTL	397.1	1326.7	0.40
UNIQUAC	212.0	66.64	

The group-contribution UNIFAC parameters for the interactions  $\text{CH}_2 / \text{CF}_2$ , and  $\text{CH}_2=\text{CH} / \text{CF}_2$ , determined by using the same technique are presented in table 4.

The root mean square deviations (RMSD) between the experimental and calculated values of  $P$ ,  $T$  and  $y$  are shown in Table 5.

TABLE 4  
UNIFAC group interaction parameters,  $a_{mn}$  (K)

	$\text{CH}_2$	$\text{CH}_2=\text{CH}$	$\text{CF}_2$
$\text{CH}_2$	0	-200.0 <sup>a</sup>	10.19
$\text{CH}_2=\text{CH}$	2520 <sup>a</sup>	0	253.7
$\text{CF}_2$	127.4	83.07	0

<sup>a</sup> Parameters obtained from Fredenslund et al. (1977)

TABLE 5  
Root mean square deviations between experimental and calculated data

Model	$P$ (kPa)	$T$ (K)	$y$
<i>Perfluoromethylcyclohexane / n-hexane at 328.15 K</i>			
Van-Laar	0.06	0.18	0.013
Margules	0.08	0.23	0.013
Wilson	0.07	0.19	0.012
NRTL	0.04	0.12	0.011
UNIQUAC	0.06	0.17	0.013
UNIFAC	0.14	0.37	0.018
<i>Perfluoromethylcyclohexane / n-hexane at 93.3 KPa</i>			
Van-Laar	0.05	0.12	0.008
Margules	0.11	0.27	0.010
Wilson	0.10	0.23	0.012
NRTL	0.02	0.05	0.007
UNIQUAC	0.09	0.20	0.008
UNIFAC	0.12	0.30	0.009
<i>Perfluoromethylcyclohexane / 1-hexene at 328.15 K</i>			
Van-Laar	0.07	0.19	0.007
Margules	0.13	0.35	0.012
Wilson	0.11	0.28	0.009
NRTL	0.12	0.31	0.009
UNIQUAC	0.07	0.19	0.007
UNIFAC	0.12	0.26	0.006
<i>Perfluoromethylcyclohexane / 1-hexene at 93.3 KPa</i>			
Van-Laar	0.06	0.13	0.012
Margules	0.13	0.30	0.014
Wilson	0.13	0.30	0.013
NRTL	0.04	0.09	0.011
UNIQUAC	0.09	0.20	0.011
UNIFAC	0.13	0.32	0.008



The results of correlation show that all the equations studied are similar in the representation of data.

All the systems show positive deviations from the Raoult's law. Figure 6 represents a comparison of experimental activity

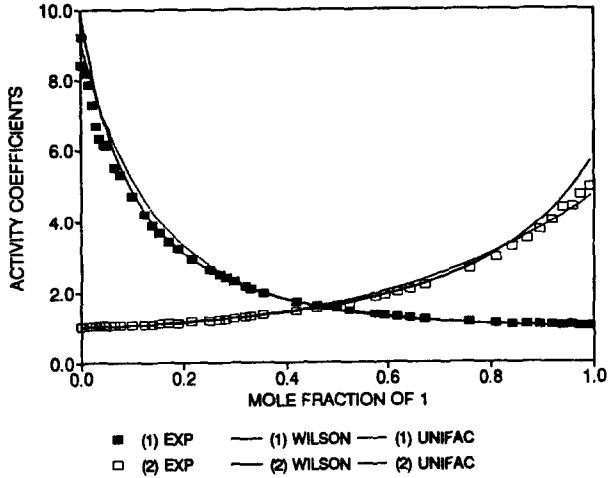


Fig. 6 Activity coefficients for perfluoromethylcyclohexane / n-hexane at 328.15 K

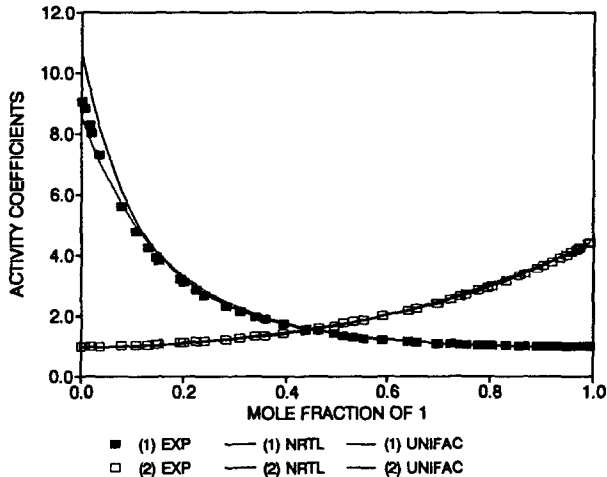


Fig. 7 Activity coefficients for perfluoromethylcyclohexane / n-hexane at 93.3 KPa.

coefficients with those calculated using the Wilson and UNIFAC equations for the system perfluoromethylcyclohexane / n-hexane at 328.15 K. In Figure 7 comparisons are made between the experimental activity coefficients and those obtained by using the Wilson and the UNIFAC equations for the binary perfluoromethylcyclohexane / n-hexane at 93.3 KPa. Figure 8 shows a comparison of experimental activity coefficients with those calculated using the NRTL and UNIQUAC equations for the system perfluoromethylcyclohexane / 1-hexene at 328.15 K. In Figure 9 comparisons are made between the experimental activity coefficients and those obtained by using the Wilson and the UNIFAC equations for the binary perfluoromethylcyclohexane / 1-hexene at 93.3 KPa. There is a good agreement between calculated and experimental values of activity coefficients for all the systems.

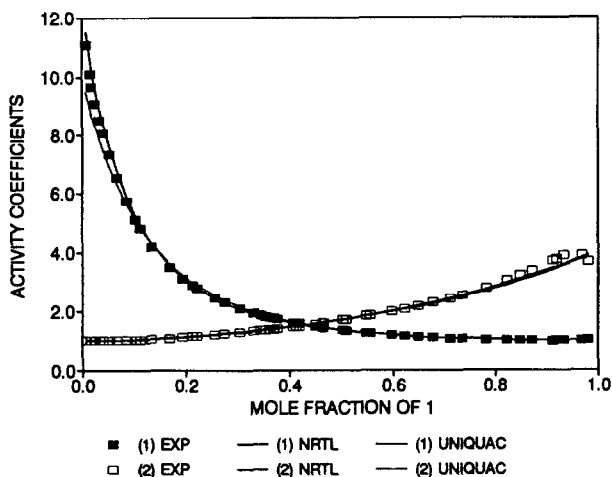


Fig. 8. Activity coefficients for perfluoromethylcyclohexane / 1-hexene at 328.15 K

## CONCLUSIONS

Consistent experimental vapor-liquid equilibrium data for some binary mixtures consisting of perfluoromethylcyclohexane and n-hexane or 1-hexene have been reported. The data have been correlated in terms of different models used for the description of liquid phase activity coefficients. The results show that the models are appropriate and give almost identical deviations.

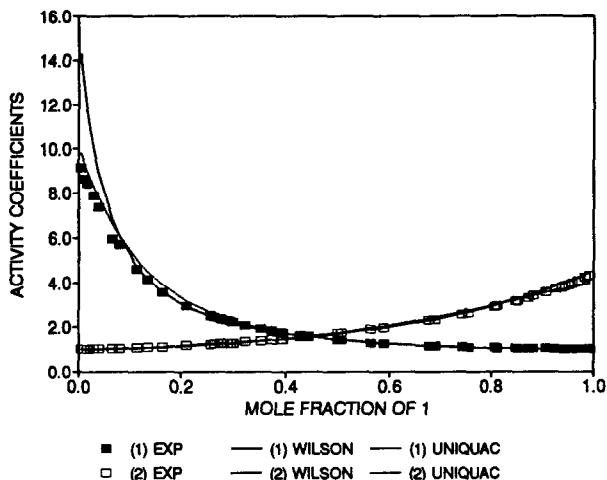


Fig. 9. Activity coefficients for perfluoromethylcyclohexane / 1-hexene at 93.3 kPa.

#### ACKNOWLEDGMENTS

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#### LIST OF SYMBOLS

$A_{12}, A_{21}$	binary interaction parameters
$P$	pressure (kPa)
$T$	temperature (K)
$x_i$	liquid phase mole fraction of component $i$
$y_i$	vapor phase mole fraction of component $i$
$\alpha_{12}$	NRTL nonrandomness parameter
$\gamma_i$	activity coefficient of component $i$

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