in their measurements; the effect of temperature is generally too weak to allow a precise calculation of excess partial molar enthalpies at infinite dilution. The activity coefficients for paraffinic and olefinic hydrocarbons were about 1 in all of the stationary phases investigated, except in those containing the keto and hydroxyl groups, where they are obviously higher for *n*-paraffins than for 1-olefins with the same number of C atoms. The hydroxyl group clearly shows its influence, the activity coefficients of the paraffins being higher in these phases than in the phases containing the keto group (polar phases), but is unable to give hydrogen bonding.

The behavior of aromatic hydrocarbons in the various phases is similar to that of the other hydrocarbons (especially the olefins). On the other hand it is to be noted that benzene shows activity coefficients in the chloro phases much smaller than 1 (0.65): this indicates the presence of remarkable "association" phenomena in the liquid phase. The activity coefficients of chloroparaffins are generally about 1; they are lower than 1 in the keto and chloro phases (in a similar way to the paraffins in paraffinic phases) and slightly higher than 1 in the paraffinic and olefinic phases. The only significant difference in the behavior of the chloroparaffins can be observed in the hydroxyl phases, where the activity coefficients are markedly higher than 1 (1.12-1.70).

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Activity Coefficients at Infinite Dilution by Gas-Liquid Chromatography. 2. Polar Compounds in Organic Solvents

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Activity coefficients at infinite dilution of acetates, alcohols, nitriles, nitromethane, chloroform, and tetrachloromethane in 12 stationary phases were determined by gas chromatography. The stationary phases employed were *n*-hexadecane, *n*-octadecane, *n*-tetracosane, 1-hexadecene, 1-octadecene, 1-chlorohexadecane, 1-chlorooctadecane, 1-dodecanol, 1-tetradecanol, 10-nonadecanone, 2-dodecanone, and 9-heptadecanone. The investigation was carried out at temperatures ranging from 30 to 80 °C.

Introduction

As was emphasized in the first part of this work (*1*), the purpose of the investigation was to provide a data basis for the calculation of interaction parameters through the UNIFAC group contribution method (*2*). To this end it is necessary, first of all, to study the interactions between the nonpolar CH_2 group and the other organic groups and then the interactions between the polar groups.

The present paper reports the activity coefficients at infinite dilution for acetates, alcohols, nitriles, chloroform, tetrachloromethane, and nitromethane in stationary phases of paraffinic and olefinic hydrocarbons, alcohols, ketones, and *n*-chloroparaffins.

Experimental Section

The activity coefficients at infinite dilution were calculated according to ref *3*. The operating conditions are the same as those reported in ref *4*. The accuracy of the activity coefficients at infinite dilution is ±2.5%; this value was evaluated by taking into account the errors in the measurement of the experimental quantities (retention time, inlet and outlet pressure, amount of stationary phase, flow rate of the carrier gas, and temperature). The solutes (Table I) and the stationary phases

Table I. Solute Components

solute no.	compd	solute no.	compd
1	methyl acetate	8	1-butanol
2	ethyl acetate	9	nitromethane
3	*n*-propyl acetate	10	acetonitrile
4	*n*-butyl acetate	11	propionitrile
5	methanol	12	*n*-butyronitrile
6	ethanol	13	chloroform
7	1-propanol	14	tetrachloromethane

Table II. Activity Coefficients at Infinite Dilution in *n*-Hexadecane

solutes	temp, °C	39.0	44.0
2		2.51	2.69
3		2.34	2.56
4		2.13	2.38
5		21.53	29.44
6		20.35	23.60
7		18.14	18.46
8		18.31	17.52
9		4.76	5.86
10		21.61[a]	17.61[b]

[a] 32.1 °C. [b] 42.2 °C.

Table III. Activity Coefficients at Infinite Dilution in *n*-Octadecane

solutes	temp, °C	51.0	60.0	69.1	79.0
2		2.47	2.44	2.39	2.31
3		2.31	2.28	2.22	2.13
4		2.16	2.13	2.09	2.03
5		22.66	21.53	19.68	16.34
6		18.79	16.75	14.58	12.16
7		14.51	12.53	10.81	9.01
8		13.63	11.49	9.58	8.10
9		5.49	5.56		6.10
10		15.91	12.69^a	11.18^b	9.51^c

^{a} 61.4 °C. ^{b} 70.5 °C. ^{c} 80.5 °C.

Table IV. Activity Coefficients at Infinite Dilution in *n*-Tetracosane

solutes	temp, °C	51.0	60.1	70.2	82.0
2		1.87		1.84	1.73
3		1.81		1.71	1.54
4		1.73	1.76	1.62	1.53
5			19.45	15.55	11.99
6		13.76	13.60	10.82	7.64
7		10.70	10.19	7.87	5.92
8		10.34	9.24	7.12	5.44
9		4.03	4.26	3.87	3.39
10		13.63	10.88	9.57	8.29^a
13		0.76	0.76	0.73	0.72^a
14		0.65	0.63	0.62	0.61^a

^{a} 80.3 °C.

Table V. Activity Coefficients at Infinite Dilution in 1-Hexadecene

solutes	temp, °C	42.0	48.2	57.8	66.2
2		2.13	2.18	2.18	2.20
3		2.04	2.16	1.99	2.03
4			1.98	1.84	1.89
6		13.78	12.17	11.04	9.97
7		14.50	12.75	10.08	8.99
8		13.06	11.79	9.22	8.27
13		0.89^a	0.87^b	0.86^c	0.85^d
14		0.80^a	0.80^b	0.78^c	0.78^d

^{a} 39.7 °C. ^{b} 46.5 °C. ^{c} 53.5 °C. ^{d} 60.1 °C.

Table VI. Activity Coefficients at Infinite Dilution in I-Octadecene

solutes	temp, °C	42.0	51.0	62.0	71.0
2		1.94	1.84	1.84	1.85
3		1.77	1.61	1.69	1.66
4		1.60	1.53	1.57	1.56
6		14.82	11.92	10.62	7.56
7		11.39	9.24	7.91	6.79
8		10.74	8.56	7.24	6.24
13		0.86	0.83	0.81^a	0.80^b
14		0.76	0.75	0.74^a	0.74^b

^{a} 60.9 °C. ^{b} 70.1 °C.

Table VII. Activity Coefficients at Infinite Dilution in 1-Chlorohexadecane

solutes	temp, °C	44.0	50.2	55.5
2		1.58	1.60	1.58
3		1.45	1.46	1.44
5		16.42	11.90	14.00
6		13.18	12.59	10.80
7		10.10	9.25	8.20
8		9.35	8.49	7.41
9		7.24	6.96	6.57
13		0.72^a	0.72^b	0.72
14		0.74^a	0.74^b	0.73

^{a} 42.2 °C. ^{b} 47.7 °C.

Table VIII. Activity Coefficients at Infinite Dilution in 1-Chlorooctadecane

solutes	temp, °C	41.0	48.0	55.0	64.2
2		1.62	1.62	1.56	1.42
3		1.52	1.52	1.45	1.34
4			1.43	1.37	1.26
5		15.24	13.24	12.15	9.73
6		11.79	10.68	9.37	7.72
7		9.23	8.62	7.38	6.02
8		9.07	8.13	7.00	4.02
9		2.17	2.13	2.06	1.93
13		0.69^a	0.69^b	0.67^c	
14		0.71^a	0.70^b	0.69^c	

^{a} 42.4 °C. ^{b} 50.8 °C. ^{c} 60.6 °C.

Table IX. Activity Coefficients at Infinite Dilution in 1-Dodecanol

solutes	temp, °C	35.0	42.8	53.0	60.0
1		2.50	2.40	2.01	1.93
2		1.91		1.84	1.77
3			1.97	1.77	1.67
4			1.89	1.75	1.71
9		10.33	8.75	7.43	6.72
10		7.46	6.30	5.35	4.40
11		5.35	4.66	4.13	3.78
12			4.06	3.82	3.28
13		1.00	0.97	0.96	0.95
14		1.48	1.40	1.36	1.32

Table X. Activity Coefficients at Infinite Dilution in 1-Tetradecanol

solutes	temp, °C	44.8	56.0	65.0	75.8
1		1.99	1.82	1.75	1.55
2		1.79	1.65	1.54	1.38
3			1.81	1.47	1.30
4			1.52	1.41	1.26
9		7.98	6.75	5.74	4.55
10		5.76	4.97	4.35	3.65
11		4.26	3.77	3.39	2.89
12			3.26	2.91	2.51
13		0.84	0.86	0.85	0.82
14		1.16	1.15	0.97	1.00

Table XI. Activity Coefficients at Infinite Dilution in 2-Dodecanone

solutes	temp, °C	36.0	40.8	50.4
1		1.64	1.53	1.58
2		1.45	1.39	1.44
3		1.39	1.33	1.36
5		3.97^a	3.59	3.66
6		5.39^b	3.38	3.35
7		3.04	2.89	2.76
9		2.56	2.17	2.21
10		2.56^b	2.39	2.42
11		1.98	1.90	1.94
13		0.39^a	0.40	0.44
14		0.97^a	0.94	0.99

^{a} 34.8 °C. ^{b} 35.4 °C.

used were reagent-grade products obtained from Fluka, C. Erba, and Baker.

Results and Discussion

The activity coefficients determined experimentally are reported in Tables II–XIII. Very few data of activity coefficients at infinite dilution of polar compounds in the stationary phases herein investigated are given in the literature (*4–6*), and often they are not corrected for nonideality in the gas phase. A comparison could be possible on the basis of the specific retention volumes of some alcohols in long paraffins, chloro-

Table XII. Activity Coefficients at Infinite Dilution in 9-Heptadecanone

solutes	temp, °C	57.7	60.8	70.8
1		1.36	1.33	1.33
2			1.26	1.24
3			1.19	1.18
4		1.10	1.12	1.12
5		3.26	3.22	3.05
6		3.12		2.83
7		2.68	2.66	2.45
8		2.49	2.48	2.29
9		2.31	2.35	2.22
10		2.44	2.45	2.39
11		1.97	1.99	1.97
12		1.68	1.71	1.68
13		0.37	0.38	0.42
14		0.68	0.71	0.73

Table XIII. Activity Coefficients at Infinite Dilution in 10-Nonadecanone

solutes	temp, °C	61.4	70.6	80.8	91.5
1		1.28	1.24	1.21	1.18
2		1.18	1.17	1.14	1.13
3		1.12	1.09	1.12	1.08
4		1.05	1.04	1.03	1.01
5		3.12	2.94	2.65	2.42
6		2.92	2.71	2.42	2.12
7		2.45	2.25	2.06	1.90
8		2.33	2.10	1.92	1.75
9		2.31	2.21	2.11	1.98
10		2.52	2.35	2.28	2.15
11		1.98	1.91	1.84	1.78
12		1.68	1.64	1.60	1.53
13		0.37	0.38	0.41	0.42
14		0.65	0.65	0.65	0.66

paraffins, and ketones (*7–10*); where this comparison was possible, the agreement was quite good.

One of the few possibilities for comparing our data with those given in the literature is reported in Table XIV, where the activity coefficients at infinite dilution of alcohols in di-*n*-octyl ketone at 70 °C given by Martire et al. (*11*) are compared with the activity coefficients of the same solutes in heptadecanone and in nonadecanone at 70.7 °C presented in this work. It is worth noting that the agreement is very good.

In all of the stationary phases tested, the values were determined at three or four temperatures (depending also on the physical characteristics of the substances used). In some cases, the solutes having relatively low vapor pressure were not injected at the lower temperatures because the retention times would have been very high and the results would not have been precise.

Generally, the activity coefficients at infinite dilution decrease with increasing temperature: this means that the considered mixtures have a positive excess partial molar enthalpies at infinite dilution.

This evaluation is made on a qualitative basis since only in very few cases is the variation of activity coefficients with temperature determinable, allowing a significant evaluation of the excess partial molar enthalpy.

Table XIV. Comparison between Literature and Experimental Data

	heptadecanone (70 °C)	di-*n*-octyl ketone (70.8 °C)	nonadecanone (70.7 °C)
methanol	3.05		2.94
ethanol	2.83	2.84	2.71
1-propanol	2.45	2.44	2.25
1-butanol	2.29	2.16	2.10

As regards the behavior of the mixtures investigated, the following considerations can be made. Acetates have the highest activity coefficients in hydrocarbon stationary phases (paraffins and olefins) and the lowest in chloro compounds. Alcohols show particularly high activity coefficients in hydrocarbon stationary phases, and this accounts for a partial miscibility for the lower terms of the homologous series (e.g., ethanol). A similar behavior is observed for nitriles; in fact, acetonitrile shows a partial miscibility in *n*-heptane. Chloroform and tetrachloromethane are the only compounds which have activity coefficients lower than 1 in the various stationary phases investigated.

Conclusions

On the basis of the experimental data reported previously (*1*) and in the present paper, it is possible to define the interactions between the 12 following groups (according to the definition given by Fredeslund (*2*)): CH_3, C═C, ACH, $ACCH_2$, OH, CH_3-OH, CH_2CO, CCN, CCl, CCl_4, $CHCl_3$, CH_3NO_2.

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