agreements are demonstrated in Figures 4-6, where the lines represent the calculated values from eq 4-6, respectively.

With these developed parameters the solubility of oxalic acid dihydrate was calculated for the test solutions and listed as the calculated values in Table I. There is good agreement between calculated and observed values. Therefore, eq 1 can be used as a model to predict the solubility of the oxalic acid in mixtures of nitric and sulfuric acids when the concentration of these mineral acids is known.

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Received for review March 17, 1982. Accepted June 2, 1982.

Activity Coefficients at Infinite Dilution by Gas-Liquid Chromatography. 1. Hydrocarbons and *n*-Chloroparaffins in Organic Solvents

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Activity coefficients at infinite dilution of paraffins, olefins, aromatics, and *n*-chloroparaffins 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.

Table I. Solute Components

solute no.	compd	solute no.	compd
1	*n*-pentane	10	methylcyclohexane
2	*n*-hexane	11	ethylcyclohexane
3	*n*-heptane	12	benzene
4	*n*-octane	13	toluene
5	1-pentene	14	ethylbenzene
6	1-hexene	15	1-chloropropane
7	1-heptene	16	1-chlorobutane
8	1-octene	17	1-chloropentane
9	cyclohexane	18	1-chlorohexane

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

solutes temp, °C	31.7	42.2	51.3
2	0.91	0.92	0.87
3	0.93	0.93	0.93
5		0.92	
6	0.95	0.93	0.92
7	0.96	0.96	0.94
12	1.04[a]	1.03[b]	
13	1.05[a]	1.04[b]	
16	1.18	1.16	1.12
17	1.19	1.17	1.13

[a] 38.9 °C. [b] 43.8 °C.

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

solutes temp, °C	51.4	61.4	70.5	80.5
2	0.85	0.86	0.88	0.86
3	0.86	0.89	0.89	0.88
6	0.85		0.88	0.86
7	0.88	0.90	0.90	0.89
12	1.03	1.03[a]	1.03[b]	1.02[c]
13	1.03	1.04[a]	1.04[b]	1.04[c]
14		1.12[a]	1.13[b]	1.13[c]
16	1.02	1.03	1.05	0.99
17	1.02	1.05	1.03	1.02

[a] 60.0 °C. [b] 68.8 °C. [c] 78.8 °C.

Introduction

Fluid-phase equilibrium data at low pressures are usually interpreted through excess functions. This means that it is possible to calculate the compositions of the phases at equilibrium from the excess quantities (activity coefficients) for the liquid mixtures and, vice versa, the excess quantities of the liquid phase from the experimentally determined compositions of the phases. In both cases, it is generally useful to have a model which expresses the variation of the excess quantity as a function of various variables (temperature, pressure, and composition), so that the effect of such quantities on equilibrium can be evaluated correctly.

In the building up of a thermodynamical model, the effect of pressure is usually neglected and that of temperature is considered a secondary one. In other words, the model is built up principally to provide the composition dependence of the excess quantity, primarily of excess free energy. The effect of the temperature is often added subsequently, by considering the temperature dependence of the parameters which are included in the model.

The majority of liquid-solution models contain two arbitrary parameters per binary pair. Generally, such parameters are not determinable a priori.

Even if we consider the limitations involved in the use of binary constants alone, the calculation of any equilibrium for a multicomponent system (n = number of components) will require the knowledge of $n(n - 1)$ interaction parameters. Even when we use methods which allow rapid and accurate experimental determinations, the amount of work required will obviously be enormous, even if we are "lucky" enough to have at our disposal data for some binary mixtures. In view of these considerations, the methods based on group contribution come into use because they allow the infinite variety of organic compounds to be reduced to a large but finite number of organic constituent groups. The knowledge of the binary parameters relative to the groups, and not that relative to the components, is needed for prediction of the behavior of any "homologous" mixture (i.e., a mixture made up of compounds with the same groups). The applicability of such methods is wider when the number of "characterized" groups is large or when the interaction parameters of these groups with all of the other groups are known. The currently most used group contribution method is the UNIFAC method (*1*), where the parameters are evaluated through the reduction of experimental liquid-vapor equilibrium data. Unfortunately, even in the latest revision of UNIFAC parameters (*2*), there are still many "blanks", because the data are either lacking or not sufficiently accurate. In effect, in some cases the physical nature of some substances makes it quite difficult to carry out accurate measurements of liquid-vapor equilibrium. In such cases, it can be convenient to obtain UNIFAC parameters through the reduction of particular liquid-vapor equilibrium data, such as activity coefficients at infinite dilution determined by gas-liquid chromatography.

This last problem will not be dealt with in the present paper, which, together with another one to follow (*3*), has been aimed

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

solutes temp, °C	51.3	60.6	70.4	80.3
1	0.73	0.73	0.74	0.73
2	0.78	0.78	0.77	0.76
3	0.80	0.80	0.79	0.78
5	0.77	0.75	0.75	0.74
6	0.75	0.76	0.76	0.76
7	0.81	0.80	0.79	0.79
12	0.75	0.80	0.76	0.71^a
13	0.76	0.81	0.77	0.73^a
14	0.85	0.89	0.85	0.79^a
16	0.94	0.89	0.86	0.83
17	0.94	0.91	0.88	0.86

[a] 82.0 °C.

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

solutes temp, °C	39.5	46.5	53.7	60.1
1	0.93	0.93	0.92	0.93
2	0.95	0.94	0.94	0.94
3	0.97	0.96	0.96	0.95
5	0.91	0.90	0.90	0.91
6	0.93	0.92	0.91	0.92
7	0.95	0.94	0.93	0.94
12		1.06^a	1.05^b	1.09^c
13		1.06^a	1.04^b	1.09^c
14		1.15^a	1.10^b	1.07^c
15	1.06	1.04	1.01	1.01
16	1.06	1.04	1.03	1.01
17	1.07	1.06	1.03	1.03

[a] 48.2 °C. [b] 57.8 °C. [c] 66.2 °C.

Table VI. Activity Coefficients at Infinite Dilution in 1-Octadecene

solutes temp, °C	41.5	51.5	61.0	70.1
1	0.90	0.88	0.90	0.88
2	0.92	0.91	0.90	0.90
3	0.95	0.94	0.92	0.92
5	0.87	0.87	0.85	0.85
6	0.90	0.89	0.86	0.87
7	0.92	0.91	0.90	0.90
12	0.86	0.82	0.86	0.86
13	0.83	0.80	0.85	0.86
14		0.74	0.90	0.93
15	1.00	0.98	0.96	0.94
16	1.02	0.99	0.97	0.96
17	1.03	1.01	0.99	0.98

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

solutes temp, °C	40.1	47.8	55.2	61.2
1	1.04	1.01	1.01	0.99
2	1.06	1.03	1.02	1.02
3	1.08	1.05	1.05	1.04
5	0.95	0.92	0.92	0.91
6	0.98	0.95	0.94	0.94
7	1.01	0.97	0.97	0.96
12		0.77^a	0.79^b	0.78^c
13		0.75^a	0.75^b	0.76^c
15	0.87^d	0.85	0.84	0.84
16	0.87^d	0.86	0.86	0.86
17	0.89^d	0.87	0.87	0.87

[a] 44.0 °C. [b] 50.2 °C. [c] 55.5 °C. [d] 41.9 °C.

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

solutes temp, °C	42.4	50.8	60.6	70.3
1	0.97	0.96	0.96	0.96
2	1.00	0.99	0.97	0.96
3		1.01	1.00	0.99
5	0.89	0.89	0.88	0.87
6	0.92	0.92	0.91	0.90
7		0.93	0.93	0.93
12		0.80^a	0.77^b	0.72^c
13		0.80^a	0.78^b	0.73^c
14		0.88^a	0.81^b	0.80^c
15	0.83	0.82	0.81	0.80
16		0.83	0.82	0.82
17		0.85	0.84	0.83

[a] 47.9 °C. [b] 54.8 °C. [c] 64.0 °C.

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

solutes temp, °C	35.0	42.8	53.0	60.0
1	1.92	1.90	1.89	1.84
2	2.13	2.14	2.05	1.99
3	2.28	2.25	2.15	2.12
4		2.41	2.24	2.22
5	1.79	1.72	1.66	1.69
6	1.98	1.91	1.83	1.83
7	2.12	2.07	1.99	1.95
8		2.20	2.09	2.04
9	1.71	1.66	1.57	1.58
10	1.81	1.77	1.69	1.66
11		1.87	1.77	1.76
12	2.07	1.94	1.79	1.72
13		1.56	1.48	1.45
14		1.79	1.64	1.41
15	1.76	1.75	1.56	1.55
16	1.91	1.79		1.67
17		1.89	1.75	1.71

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

solutes temp, °C	44.8	56.1	65.1	75.8
1	1.61	1.62	1.62	1.56
2	1.70	1.73	1.79	1.64
3	1.83	1.82	1.77	1.67
4		1.91	1.86	1.73
5	1.47	1.49	1.44	1.36
6	1.63	1.65	1.58	1.50
7	1.70	1.69	1.64	1.55
8		1.77	1.72	1.61
9	1.35	1.35	1.30	1.23
10	1.41	1.42	1.38	1.30
11		1.50	1.46	1.37
12	1.27	1.53	1.44	1.32
13		1.27	1.22	1.13
14		1.42	1.35	1.24
15	1.40	1.37	1.39	1.25
16	1.51	1.48	1.40	1.34
17		1.52	1.47	1.35

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

solutes	temp, °C	33.8	42.5	51.7
1		1.45	1.48	1.43
2		1.52	1.56	1.49
3			1.62	1.55
5		1.21	1.25	1.20
6		1.25	1.30	1.25
7			1.37	1.31
12		0.89	0.89	0.91
13			0.90	0.92
15		0.81	0.85	0.82
16		0.85	0.90	0.87
17				0.90

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

solutes	temp, °C	56.7	60.8	70.8	82.7
1		1.12	1.07	1.08	1.02
2		1.15	1.10	1.12	1.05
3		1.20	1.14	1.14	1.08
4		1.25	1.20	1.19	1.12
5		0.99	0.96	0.96	0.88
6		1.03	1.01	0.99	0.93
7		1.08	1.05	1.02	0.98
8		1.11	1.09	1.05	1.01
12		0.70[a]	0.69	0.69	
13		0.68[a]	0.71	0.71	
14		0.75	0.78	0.78	
15		0.76	0.75	0.74	0.76
16		0.79	0.78	0.75	0.74
17		0.82	0.80	0.79	0.75
18			0.85	0.83	0.79

[a] 57.7 °C.

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

solutes	temp, °C	65.3	70.7	80.5	89.6
1		1.02	1.00	0.99	0.96
2		1.04	1.05	1.02	1.01
3		1.08	1.10	1.04	1.03
4			1.13	1.09	1.07
5		0.90	0.91	0.89	0.85
6		0.93	0.92	0.92	0.90
7		0.97	0.98	0.95	0.94
8			1.00	0.99	0.98
12		0.63[a]	0.64	0.64	0.64[b]
13		0.65[a]	0.65	0.66	0.66[b]
14		0.71[a]	0.71	0.72	0.71[b]
15		0.71	0.70	0.73	0.69
16		0.73	0.72	0.73	0.72
17		0.76	0.77	0.75	0.74
18			0.80	0.79	0.78

[a] 61.4 °C. [b] 91.5 °C.

at providing the necessary data for such calculations. For this purpose, simple stationary phases, i.e., phases containing only one functional group other than CH_3 and CH_2, where chosen. The activity coefficients for hydrocarbon systems (where the solute and the stationary phase are paraffins) were determined so that they can be used as a reference. In this first paper, the data relative to hydrocarbons and *n*-chloroparaffins in *n*-hexadecane, *n*-octadecane, *n*-tetracosane, 9-heptadecanone, 10-nonadecanone, 2-dodecanone, 1-chlorohexadecane, 1-chlorooctadecane, 1-hexadecene, 1-octadecene, 1-dodecanol, and 1-tetradecanol are reported.

Experimental Section

A Fractovap Model ATC/t (Carlo Erba) thermal conductivity chromatograph was used as the GLC apparatus. The column temperature was controlled to within ±0.2 °C and measured by means of an electronic thermometer (Avo Comark). The carrier gas (hydrogen) flow rate was measured by means of a soap-film meter. The internal pressure gradient was measured to within ±1 mmHg by a mercury manometer. The outlet pressure was atmospheric. The quantities of solutes injected were 0.2 μL. The operating conditions are summarized as follows: stainless-steel column (2 m long, 4-mm internal diameter); support, 60–80 mesh Chromosorb W (C. Erba) acid washed and silanized; quantitative ratio of support to stationary phase = 3:1 (by weight); internal pressure gradient, 250–270 mmHg. The solutes and the stationary phases used were reagent-grade products obtained from Fluka, C. Erba, and Baker. The activity coefficients at infinite dilution were calculated according to 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 measurements of the experimental quantities (retention time, inlet and outlet pressure, amount of stationary phase, flow rate of the carrier gas, and temperature).

Results and Discussion

Tables I–XIII report the activity coefficients at infinite dilution for solutes in the 12 stationary phases investigated. For each solute–stationary phase pair, the activity coefficients were determined at three or four temperatures, to allow the experimental data to be better evaluated and verified.

A comparison with literature data is possible only in a few cases. This is due to the fact that the data reported in the literature are scanty, many of them are not corrected for the nonideality in the gas phase, often the data are not relative to a homologous series of solutes, and the operative temperatures are not the same.

However, activity coefficients at infinite dilution of hydrocarbons in *n*-hexadecane, *n*-octadecane, and *n*-tetracosane are given in ref *5*–*11*, those in chloroparaffins in ref *9*, those in nonadecanone in ref *12*, and those in olefins in ref *13*. The agreement between the experimental data reported in this work and those given in the literature is quite good (Table XIV).

As regards the activity coefficients at infinite dilution of chloroparaffins in tetracosane (*11*), the agreement is very good, the differences being in the same range as the experimental error.

The variations of activity coefficients with temperature are, in general, in the same range as the experimental error involved

Table XIV. Comparison between Experimental and Literature Data

	1-chlorohexadecane		*n*-octadecane		nonadecanone	
	ref *11* (45 °C)	this work (44.0 °C)	ref *8* (80 °C)	this work (80.5 °C)	ref *12* (60 °C)	this work (65.3 °C)
n-heptane	1.057	1.05			1.067	1.08
toluene	0.749	0.75				
n-hexane			0.84	0.88	1.017	1.04
1-hexene			0.84	0.86		

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).

Acknowledgment

We appreciate the contributions of M. Cerovaz and M. Gasperini.

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Received for review July 14, 1981. Revised manuscript received Febrarury 3, 1982. Accepted May 10, 1982. This work was carried out with the support of "Progetto Finalizzato C.N.R. Chimica Fine e Secondaria" (C.N.R.—Rome) and of NATO.

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.