Table XI. New Group Interaction Parameters for UNIFAC and Comparison with the Old Parameters

	old parameters[a]	new parameters[b]
AAD($\Delta\gamma_1/\gamma_1$)	0.050	0.038
AAD($\Delta\gamma_2/\gamma_2$)	0.033	0.020

[a] $a(CH_2/CHO) = 677.00$, $a(CHO/CH_2) = 505.70$.
[b] $a(CH_2/CHO) = 618.8$, $a(CHO/CH_2) = 2261.0$.

The new parameters are shown in Table XI, along with the comparison of activity coefficients calculated from both the previous parameters based only on propionaldehyde/cyclohexane data (*17*), and the new parameters. As might be expected, the fit of the *n*-butyraldehyde and isobutyraldehyde data is better with the new parameters but is worse for the mixture containing propionaldehyde. Clearly, to obtain the best possible parameters for the aldehyde/hydrocarbon functional-group interactions, a regression of data for many systems is needed.

Conclusions

Previously unavailable vapor–liquid equilibrium data for three aldehyde/hydrocarbon systems were measured. These data are themselves of potential use in engineering design and also will be of use in the estimation of more accurate group interaction parameters in the UNIFAC method and other functional-group methods for $CHO-CH_2$ and CH_2-CHO interactions. Minimum-boiling azeotropes were observed for the *n*-pentane/propionaldehyde system at 40 °C and the *n*-butyraldehyde/*n*-heptane system at 45 and 70 °C.

Acknowledgment

We thank Dr. B. Gutsche and Professor H. Knapp (Technical University of Berlin) for their advice and assistance in setting up the experimental equipment used here.

Glossary

A, *B*, *C*	Antoine constants (eq 1)
B	second virial coefficient, J/g-mol
C	number of components
d_4	density relative to that of water at 4 °C, g/mL
f	standard-state fugacity of liquid (eq 4), mmHg
G^e	excess Gibbs free energy, J/mol
n_D	refractive index
P	total pressure, mmHg
R	gas constant
T	temperature, °C
v	molar liquid volume, cm^3/g-mol
x	liquid-phase mole fraction
y	vapor-phase mole fraction
γ	activity coefficient
ϕ	fugacity coefficient (eq 3)
σ	standard deviation
Δ	difference between the experimental and calculated values
AAD	absolute average deviation
rmsd	root mean square deviation
nbp	normal boiling point, °C

Subscripts

i	component *i*

Superscripts

exptl	experimentally measured value
calcd	calculated value
s	saturation value
o	reference-state value

Registry No. *n*-Pentane, 109-66-0; propionaldehyde, 123-38-6; *n*-heptane, 142-82-5; *n*-butyraldehyde, 123-72-8; isobutyraldehyde, 78-84-2.

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Received for review March 24, 1983. Accepted September 15, 1983. The equipment for this work was purchased with funds provided by NSF Grant CPE 8104553 to the University of Delaware and also funds from the Mobil Foundation. R.E. also is pleased to acknowledge the financial support that he received as a graduate student from the Department of Chemical Engineering of the University of Delaware.

Excess Volumes of 1,1,2,2-Tetrachloroethane + Ketone

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Excess volumes for the binary mixtures of 1,1,2,2-tetrachloroethane with methyl ethyl ketone, diethyl ketone, and methyl propyl ketone have been measured at 303.15 and 313.15 K. V^E is negative over the entire mole fraction range in all the mixtures. The negative excess volumes have been explained in terms of dipole–induced dipole interactions.

Introduction

Many attempts have been made to study molecular interactions in mixtures containing chloroalkanes (*1–4*) and ketones (*5–8*) as the components. Various thermodynamic and nonthermodynamic techniques have been used to provide evidence for the existence of weak specific interactions in the mixtures of ketones and chloroalkanes (*9–11*). The electron-

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Table I. Excess Volumes V^E of 1,1,2,2-Tetrachloroethane + Ketones at 303.15 and 313.15 K

303.15 K		313.15 K	
x	V^E, $cm^3\ mol^{-1}$	x	V^E, $cm^3\ mol^{-1}$
1,1,2,2-Tetrachloroethane + Methyl Ethyl Ketone			
0.1201	−0.330	0.1342	−0.426
0.2481	−0.566	0.2026	−0.572
0.3202	−0.645	0.2811	−0.681
0.3837	−0.684	0.3698	−0.757
0.4901	−0.707	0.4507	−0.771
0.5937	−0.675	0.5623	−0.754
0.6644	−0.621	0.6339	−0.707
0.7477	−0.517	0.6925	−0.650
0.8136	−0.412	0.7489	−0.568
0.8805	−0.286	0.8544	−0.383
1,1,2,2-Tetrachloroethane + Diethyl Ketone			
0.1428	−0.335	0.0778	−0.212
0.1902	−0.426	0.1536	−0.369
0.2469	−0.501	0.2301	−0.517
0.3131	−0.566	0.3874	−0.666
0.4136	−0.612	0.4227	−0.678
0.5208	−0.612	0.5135	−0.685
0.6415	−0.550	0.5896	−0.649
0.7217	−0.455	0.7031	−0.551
0 7825	−0.381	0.8082	−0.402
0.8755	−0.239	0.8856	−0.263
1,1,2,2-Tetrachloroethane + Methyl Propyl Ketone			
0.1347	−0.318	0.1404	−0.366
0.2138	−0.454	0.2256	−0.522
0.2827	−0.542	0.2885	−0.603
0.3471	−0.597	0.3694	−0.677
0.4149	−0.633	0.4211	−0.695
0.5002	−0.646	0.5207	−0.698
0.5993	−0.610	0.5988	−0.659
0.7099	−0.522	0.7128	−0.553
0.7905	−0.420	0.7763	−0.458
0.8802	−0.274	0.8410	−0.351

accepting properties of tetrachloroethanes and other chloroethanes have been well established earlier by several workers(*12–14*). However, no attempt has been made to study the interaction between 1,1,2,2-tetrachloroethane and ketones. Hence, we measured excess volumes for the mixtures 1,1,2,2-tetrachloroethane with ketones, which exhibit dipole–dipole interactions in the pure state. The ketones include methyl ethyl ketone, diethyl ketone, and methyl propyl ketone. The data were collected at 303.15 and 313.15 K.

Experimental Section

Excess volumes were measured by using the dilatometer described by Rao and Naidu (*15*). The mixing cell contained two bulbs of different capacities which were connected through a U-tube having mercury to separate the two components. One end of the bulb was fitted with a capillary (1-mm i.d.) and the other end of the second bulb was fixed with a ground-glass stopper. The V^E values were accurate to ±0.003 $cm^3\ mol^{-1}$.

Purification of Materials. 1,1,2,2-Tetrachloroethane (Riedel) was purified by using the procedure described earlier (*2*). Ketones were purified by the methods described by Riddick and Bunger (*16*). Methyl ethyl ketone (BDH) was treated several times with saturated potassium carbonate solution. The two layers were then separated. The ketone layer was distilled to remove water. It was then dried for 1 day over anhydrous potassium carbonate and finally fractionated. Diethyl ketone (Riedel) was dried over anhydrous sodium sulfate for 2 days and fractionally distilled. Methyl propyl ketone (BDH) was dried over potassium carbonate for 3 days, boiled for 2 h, and fractionally distilled. The purity of the samples was checked by comparing the measured densities with those reported in the literature (*17*). Densities were determined by using a bicapillary type pycnometer with an accuracy of 2 parts in 10^5.

Results

The experimental excess volumes for the three binary mixtures at 303.15 and 313.15 K are given in Table I. The dependence of V^E on composition may be expressed by an empirical equation of the form

$$V^E/(\mathrm{cm^3\ mol^{-1}}) = x(1-x)\{a_0 + a_1(2x-1) + a_2(2x-1)^2\} \tag{1}$$

where a_0, a_1, and a_2 are adjustable parameters and x is the mole fraction of 1,1,2,2-tetrachloroethane. The values of the parameters obtained by the least-squares method are included in Table II, along with the standard deviation $\sigma(V^E)$. The values of $\sigma(V^E)$ were obtained by using the equation

$$\sigma(V^E) = \left[\frac{\sum(V^E_{\mathrm{calcd}} - V^E_{\mathrm{exptl}})^2}{n-p}\right]^{1/2} \tag{2}$$

where n is the number of experimental data and p is the number of parameters.

Discussion

The data included in Table I show that V^E is negative over the entire composition range in all the mixtures at both the temperatures. The negative values of V^E are indicative of important interactions between unlike molecules. These interactions may be explained as follows. When a nonpolar molecule such as 1,1,2,2-tetrachloroethane is situated in an electric field set by the presence of a polar molecule, the ketone, a dipole is induced. The force between the permanent dipole of the ketone and the induced dipole of tetrachloroethane is always attractive. This leads to negative deviation in excess volume. The negative values of V^E fall in the following order: methyl ethyl ketone > methyl propyl ketone > diethyl ketone. Further, the data suggest that the rise in temperature results in an increase in negative values of V^E.

Table II. Values of Parameters for Eq 1 Calculated by the Method of Least Squares along with the Standard Deviation $\sigma(V^E)$

1,1,2,2-tetrachloroethane +	T/K	a_0, $cm^3\ mol^{-1}$	a_1, $cm^3\ mol^{-1}$	a_2, $cm^3\ mol^{-1}$	$\sigma(V^E)$, $cm^3\ mol^{-1}$
methyl ethyl ketone	303.15	−2.840	0.272	−0.145	0.003
diethyl ketone	303.15	−2.472	0.406	−0.019	0.005
methyl propyl ketone	303.15	−2.575	0.123	−0.158	0.003
methyl ethyl ketone	313.15	−3.102	0.396	−0.524	0.004
diethyl ketone	313.15	−2.738	0.220	−0.013	0.005
methyl propyl ketone	313.15	−2.811	0.300	−0.024	0.003

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Registry No. 1,1,2,2-tetrachloroethane, 79-34-5; methyl ethyl ketone, 78-93-3; diethyl ketone, 96-22-0; methyl propyl ketone, 107-87-9.

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Received for review February 28, 1983. Accepted August 15, 1983. N.V.C. is thankful to C.S.I.R., New Delhi, India, for the award of a Senior Research Fellowship.

Viscosity of Liquid-Phase Methyl Chloride

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A high-pressure capillary viscosimeter was used to measure the viscosity of liquid-phase methyl chloride in the temperature range from 20 to 150 °C. The constants of the apparatus were evaluated by calibration with gases of known viscosity. The precision of the measurements is estimated to be ±1% in the normal liquid range and ±5% in the critical region.

Introduction

Several sets of measurements of the viscosity of liquid-phase methyl chloride have been reported in the literature (*1–4*). With the exception of the very old data of ref *4*, results are not reported for temperatures above 50 °C. In addition, there are wide discrepancies among the several sets of data, amounting to nearly a 50% spread at temperatures in the range from 20 to 50 °C.

This paper describes the construction and calibration of a high-pressure capillary viscometer and its subsequent use to measure the viscosity of liquid-phase methyl chloride in the temperature range from 20 to 150 °C. The instrument was designed as a device of moderate precision suitable for gathering data of satisfactory accuracy for engineering purposes. It was not intended to be a primary device. The constants of the apparatus were evaluted by calibration with reference fluids of known viscosity. Parameters of the apparatus were chosen so as to minimize the capillary inlet correction.

Description of the Method

The apparatus (Figure 1) is a steady-flow capillary device similar in concept to the devices used by Flynn, Hanks, Lemaire, and Ross (*5*), by Kao, Ruska, and Kobayashi (*6*), and by Sun and Storvick (*7*). The capillary is a 141.78-mm length of fused silica chromatographic tubing with a nominal inside diameter of 200 μm supported inside a section of 3.2 mm o.d., 0.5 mm i.d. stainless steel tubing. Flow through the capillary is established by the coupled movement of two identical piston injectors driven by a synchronous motor through an adjustable gear train.

The pressure differential across the capillary is measured by a Sensotec wet/wet differential pressure transducer with a full-scale range of ±0.5 psid and nominal accuracy of ±0.5%. Total pressure is measured with a 2000 psig Heise Bourdon tube gauge accurate to ±1 psig.

Water jackets on the piston injectors maintain the temperature at 25 ∓ 0.1 °C, and the temperature of the capillary is established by a water or oil bath (depending on the temperature) within a tolerance of ±0.01 °C.

The modified Poiseuille equation for the viscosity in terms of the experimental parameters is

$$\eta = \eta_p - mX \tag{1}$$

where

$$\eta_p = \pi a^4 \Delta p / (8 Q L_{\text{eff}}) \tag{2}$$

$$X = \rho Q / (8 \pi L_{\text{eff}}) \tag{3}$$

and where a = capillary radius, Δp = pressure difference across the capillary, Q = volumetric flow rate, m = inlet correction factor, L_{eff} = effective length of capillary, and ρ = density of fluid. The slip correction, the Couette correction, and the thermal expansion of the capillary are negligible for the conditions of the experiments reported here.

According to Kestin, Sokolov, and Wakeham (*8*), the inlet correction factor m is a function of the Reynolds number. The relationship between m and the Reynolds number was evaluated from numerical calculations based on an assumed flow model for a capillary viscometer. According to ref *8*, the results of the calculations are represented with adequate accuracy in the range $2 < \text{Re} < 200$ by

$$m = m_0 + 16n/\text{Re} \tag{4}$$

where

$$m_0 = 1.17 \pm 0.03$$

$$n = 0.69 \pm 0.004$$

and where Re is the Reynolds number based on the capillary diameter. The above relationship can be used for a Reynolds numbers greater than 200 provided that laminar flow is preserved.

A second result of the work reported in ref *8* is that the effective length of the capillary is given by

$$L_{\text{eff}} = L + na$$

The result, however, is not pertinent to this investigation be-

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[†] Mound is operated for the U.S. Department of Energy under Contract No. DE-AC04-76DP00053.

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