

**Glossary**

<i>P</i>	total pressure
<i>R</i>	molar gas constant, $R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$
<i>T</i>	equilibrium temperature
<i>x</i>	mole fraction in liquid phase
<i>y</i>	mole fraction in vapor phase

**Greek Letters**

$\gamma$	activity coefficient
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**Subscripts**

<i>i, j, 1, 2</i>	components
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**Registry No.** 2,3-Dimethylbutane, 79-29-8; ethanol, 64-17-5; methanol, 67-56-1.

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## Excess Molar Volumes of Tetrachloroethene + 1,4-Dioxane + Tetrahydrofuran at 298.15 and 308.15 K<sup>†</sup>

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Densities were determined for the tetrachloroethene (1) + 1,4-dioxane (2) + tetrahydrofuran (3) system at 298.15 and 308.15 K as a function of composition. From the experimental results, molar excess volumes were calculated. Different expressions exist in the literature to predict these excess properties from the binary mixtures. The empirical correlation of Jacob and Fitzner is the best for this system.

**Introduction**

A number of researchers (1-6) have proposed equations to predict ternary excess volume data from binary excess volume data. In this work we have tested these equations using data from the binary sets and ternary system generated from the following compounds: tetrachloroethene (1), 1,4-dioxane (2), and tetrahydrofuran (3). No data could be found for the excess volume of such mixtures. However, the main reason for the present investigation has to be found in our interest in ternary liquid mixtures having a tetrachloroethene as one component and cyclic ethers as the others.

**Experimental Section**

**Materials.** The chemicals used in the present study were tetrachloroethene and tetrahydrofuran supplied by Merk and 1,4-dioxane supplied by J. T. Baker. All solvents were used from freshly opened bottles without further purification. According to the specification of the suppliers, the purities were better than 99.5 mass % for tetrachloroethene, 99.8 mass %

Table I. Densities of Pure Substances

substance	$\rho \times 10^{-3}/(\text{kg m}^{-3})$			
	298.15 K		308.15 K	
	exptl	lit.	exptl	lit.
tetrachloroethene (1)	1.6148	1.61432 <sup>a</sup>	1.5980	
1,4-dioxane (2)	1.0282	1.02797 <sup>a</sup>	1.0167	1.01635 <sup>b</sup>
tetrahydrofuran (3)	0.8823		0.8702	

<sup>a</sup>Reference 7. <sup>b</sup>Reference 8.

for tetrahydrofuran, and 99.5 mass % for 1,4-dioxane. All liquids were stored over molecular sieves (Union Carbide Type 4 A, from Fluka). The purity of the compounds was checked by determining their refractive indices and densities, which agreed well with the literature values.

Air and bidistilled water were used for densimeter calibration.

**Mixture Preparation.** All the solutions were prepared by using a Mettler H 315 balance (precision of  $1 \times 10^{-4}$  g) and air-tight stoppered bottles. The more volatile component was poured directly into the bottle. The charged bottle was closed and weighed. The second component (and the third component for ternary mixtures) was injected into the bottle through the stopper by means of a syringe. This procedure hindered any vapor loss and contamination. Hence, the possible error in the mole fraction is estimated to be lower than  $\pm 2 \times 10^{-4}$ .

**Density Measurements.** A digital densimeter (Anton Paar Model DMA 45) was employed for the determination of the densities of the pure components, the binary mixtures, and ternary mixtures. Water and air were chosen as calibrating fluids since they span a wide range and their densities are known at a high precision level. All measurements were carried out at atmospheric pressure. Pressure was measured by means of a mercury barometer. A Haake constant-temperature bath circulator was used with a temperature control interval of  $\pm 0.01$  K. Temperature was detected with a digital thermometer (Digitec) calibrated and checked at the water triple

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**Table II. Experimental Excess Molar Volumes  $V^E$  of the Three Binary Mixtures at 298.15 and 308.15 K**

mol fractn <sup>a</sup>	$V^E \times 10^{-6}/$ ( $\text{m}^3 \text{mol}^{-1}$ )		mol fractn <sup>a</sup>	$V^E \times 10^{-6}/$ ( $\text{m}^3 \text{mol}^{-1}$ )	
	298.15 K	308.15 K		298.15 K	308.15 K
Tetrachloroethene (1) + 1,4-Dioxane (2)					
0.1014	0.136	0.163	0.5477	0.315	0.354
0.1496	0.176	0.206	0.6009	0.307	0.348
0.2029	0.227	0.246	0.6500	0.291	0.328
0.2773	0.263	0.302	0.7036	0.266	0.299
0.3863	0.303	0.347	0.8022	0.200	0.227
0.4027	0.310	0.348	0.8454	0.174	0.188
0.4515	0.306	0.360	0.9009	0.129	0.146
0.4951	0.321	0.359			
Tetrachloroethene (1) + Tetrahydrofuran (3)					
0.1025	-0.029	-0.035	0.6015	-0.077	-0.088
0.1998	-0.058	-0.065	0.7052	-0.068	-0.075
0.3009	-0.072	-0.082	0.7966	-0.051	-0.062
0.3995	-0.082	-0.095	0.8929	-0.033	-0.039
0.5069	-0.075	-0.088			
1,4-Dioxane (2) + Tetrahydrofuran (3)					
0.0975	0.022	0.035	0.5996	0.063	0.070
0.2024	0.051	0.067	0.6956	0.053	0.058
0.2999	0.055	0.067	0.7911	0.045	0.057
0.3993	0.064	0.075	0.8977	0.025	0.035
0.4981	0.061	0.073			

<sup>a</sup> For the 1 + 2 and 1 + 3 systems, the mole fraction shown is  $x_1$ ; for the 2 + 3 system, the mole fraction shown is  $x_2$ .

point. The precision of the densities measured is estimated to be better than  $\pm 0.2 \text{ kg m}^{-3}$ . The excess molar volume  $V^E$  was calculated using the density measurements. The average error in  $V^E$  for all systems was smaller than  $\pm 2 \times 10^{-9} \text{ m}^3 \text{mol}^{-1}$ .

## Results and Discussion

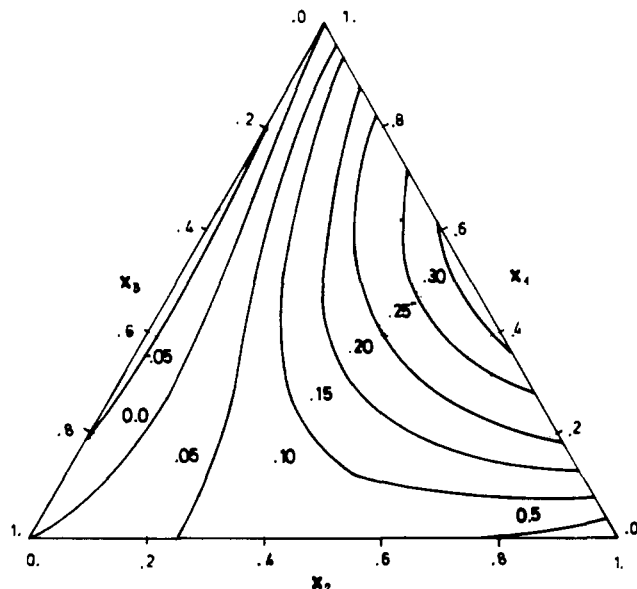
The experimental results for the pure liquids are reported in Table I, together with the values from the literature for comparison.

The experimental excess molar volumes at different mole fractions of the three binary mixtures at 298.15 and 308.15 K are reported in Table II. Molar excess volumes for the tetrachloroethene (1) + 1,4-dioxane (2) system are positive over the whole concentration range. Molar excess volumes for the tetrachloroethene (1) + tetrahydrofuran (3) mixtures are all negative, with a minimum at  $x \cong 0.5$ . The explanation of the volumetric behavior of these mixtures may be mainly attributed to structural differences of the two cyclic ethers because the molecular interactions in these mixtures are of the same kind.

The excess molar volumes of the binary systems can be represented by a Redlich-Kister equation of the form

$$V^E = x_i x_j \sum_{k=0}^n a_k (x_j - x_i)^k \quad (1)$$

where  $V^E$  represents the excess molar volume,  $x_i$  and  $x_j$  represent the mole fractions of the components  $i$  and  $j$ , and  $a_k$



**Figure 1.** Equi-value contours of excess molar volume  $V^E \times 10^6/(\text{m}^3 \text{mol}^{-1})$  for the tetrachloroethene (1) + 1,4-dioxane (2) + tetrahydrofuran (3) system at 298.15 K.

represents the polynomial coefficients. The method of least squares was used to determine the values of the coefficients. The optimum number of coefficients was ascertained from an examination of the variation of the standard error of estimate with  $n$ :

$$\epsilon = [\sum (V_{\text{obs}}^E - V_{\text{cal}}^E)^2 / (n_{\text{obs}} - n)]^{1/2} \quad (2)$$

The values for the coefficients and the standard error of estimate associated with the use of eq 2 are summarized in Table III for the three binary systems at 298.15 and 308.15 K.

From the experimental values of densities of the ternary system, molar excess volume is calculated with the following equation:

$$V^E = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{\rho} - (x_1 V_1 + x_2 V_2 + x_3 V_3) \quad (3)$$

where  $M_1$ ,  $M_2$ , and  $M_3$  are the molecular weights of the components,  $V_1$ ,  $V_2$ , and  $V_3$  are the molar volumes, and  $\rho$  is the density of the solution.

Table IV shows the experimental values of ternary densities at different mole fractions at 298.15 and 308.15 K.

Figures 1 and 2 show the experimental equal values of  $V_{123}^E$  at 298.15 and 308.15 K, respectively. The location of equi-value points in triangular plots was computed by a method in which the mole fraction of one component was kept constant while those of the other two varied in steps of 0.05 and the final refinement was attained through a binary search method. In

**Table III. Coefficients  $a_k/(10^6 \text{ m}^3 \text{mol}^{-1})$  from Equation 2 and Standard Deviations for the Binary Systems at Different Temperatures**

T/K	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$\epsilon(V^E)$
Tetrachloroethene (1) + 1,4-Dioxane (2)							
298.15	1.272	0.0516	0.0286	-0.7686	0.3932	1.033	0.004
308.15	1.450	-0.0377	-0.1372	-0.1357	0.7447		0.004
Tetrachloroethene (1) + Tetrahydrofuran (3)							
298.15	-0.3154	0.0522	-0.1598	-0.0905	0.2267		0.003
308.15	-0.3691	0.0657	-0.0568	-0.1339			0.002
1,4-Dioxane (2) + Tetrahydrofuran (3)							
298.15	0.2494	-0.0295	0.1635	0.0398	-0.2054		0.003
308.15	0.2886	-0.0713	0.1891	0.0796			0.003

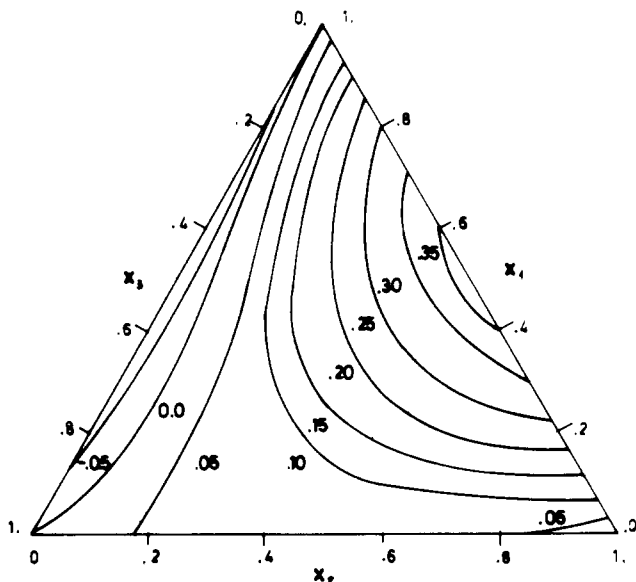


Figure 2. Equi-value contours of excess molar volume  $V^E \times 10^6 / (\text{m}^3 \text{mol}^{-1})$  for the tetrachloroethene (1) + 1,4-dioxane (2) + tetrahydrofuran (3) system at 308.15 K.

the equi-value contours of this ternary system, a small negative region at low concentrations of 1,4-dioxane is visible and affects the symmetrical disposition of contours around dominant binary mixtures containing components 1 and 2.

If interactions in a ternary,  $i + j + k$ , mixture are assumed to be closely dependent on the interactions in the constituent  $i + j$ ,  $j + k$ , and  $i + k$  mixtures, it should be possible to evaluate thermodynamic excess volumes for ternary mixtures of nonelectrolytes, when the corresponding volumes for the binary  $i + j$ ,  $j + k$ , and  $i + k$  mixtures are known.

Rastogi et al. (1) suggested a form for predicting the excess volumes of a ternary solution:

$$V_{123}^E = \frac{1}{2}[(x_1 + x_2)V_{12}^E + (x_1 + x_3)V_{13}^E + (x_2 + x_3)V_{23}^E] \quad (4)$$

In which  $V_{ij}^E$  represents the excess molar volume of the binary mixtures at composition  $x_i^\circ, x_j^\circ$ , such that

$$x_i^\circ = 1 - x_j^\circ = \frac{x_i}{x_i + x_j} \quad (5)$$

This expression is inappropriate for describing the system near infinite dilution.

Radojkovič et al. (2) takes an expression proposed by Redlich and Kister (9) for the excess free energy:

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E \quad (6)$$

where  $V_{12}^E$ ,  $V_{13}^E$ , and  $V_{23}^E$  represent the excess molar volumes with  $x_1$ ,  $x_2$ , and  $x_3$  mole fractions of the ternary system calculated with eq 1 using coefficients of Table III.

Kohler (3) proposed an equation for a ternary solution of the following form:

$$V = (x_1 + x_2)^2 V_{12}^E + (x_1 + x_3)^2 V_{13}^E + (x_2 + x_3)^2 V_{23}^E \quad (7)$$

Kohler's equation is symmetrical in that all three binary systems are treated identically. In this equation  $V_{ij}^E$  refers to the excess volumes of  $x_i^\circ, x_j^\circ$  in the binary mixtures using eq 5.

Jacob and Fitzner (4) suggested an equation for estimating the properties of a ternary solution based on the binary data

Table IV. Densities for the Tetrachloroethene (1) + 1,4-Dioxane (2) + Tetrahydrofuran (3) System at 298.15 and 308.15 K

$x_1$	$x_2$	$x_3$	$\rho \times 10^{-3} / (\text{kg m}^{-3})$	
			298.15 K	308.15 K
0.0994	0.1023	0.7983	1.0815	1.0650
0.0988	0.2113	0.6899	1.0664	1.0498
0.1015	0.2937	0.6048	1.0572	1.0404
0.0987	0.4018	0.4995	1.0406	1.0237
0.1021	0.5006	0.3973	1.0294	1.0124
0.1008	0.6072	0.2920	1.0138	0.9966
0.0991	0.6981	0.2028	0.9999	0.9828
0.0978	0.7945	0.1077	0.9856	0.9684
0.2086	0.0987	0.6927	1.1540	1.1364
0.1973	0.2012	0.6015	1.1337	1.1161
0.1980	0.2973	0.5047	1.1218	1.1042
0.2062	0.4108	0.3830	1.1127	1.0950
0.2012	0.5017	0.2971	1.0977	1.0798
0.1964	0.5962	0.2074	1.0822	1.0643
0.1932	0.7013	0.1055	1.0662	1.0483
0.3067	0.1012	0.5921	1.2161	1.1976
0.2899	0.2102	0.4999	1.1924	1.1740
0.2030	0.3062	0.4008	1.1827	1.1644
0.2911	0.3981	0.3108	1.1704	1.1519
0.2987	0.4976	0.2037	1.1633	1.1448
0.3007	0.6021	0.0972	1.1521	1.1333
0.4017	0.0971	0.5012	1.2749	1.2558
0.4112	0.2018	0.3870	1.2688	1.2498
0.3978	0.3073	0.2949	1.2488	1.2297
0.3929	0.3938	0.2133	1.2360	1.2170
0.4005	0.4981	0.1014	1.2290	1.2098
0.4972	0.0996	0.4032	1.3313	1.3119
0.4907	0.2036	0.3057	1.3166	1.2970
0.5037	0.3015	0.1948	1.3142	1.2944
0.5083	0.3962	0.0955	1.3071	1.2873
0.5915	0.1073	0.3012	1.3850	1.3653
0.5893	0.1962	0.2145	1.3751	1.3553
0.6007	0.2938	0.1055	1.3725	1.3522
0.7063	0.1015	0.1922	1.4503	1.4298
0.7018	0.1963	0.1019	1.4393	1.4187
0.8006	0.1043	0.0951	1.5018	1.4808

at composition nearest the ternary composition taking the form for excess molar volume:

$$V_{123}^E = \frac{x_1 x_2 V_{12}^E}{(x_1 + x_3/2)(x_2 + x_3/2)} + \frac{x_1 x_3 V_{13}^E}{(x_1 + x_2/2)(x_3 + x_2/2)} + \frac{x_2 x_3 V_{23}^E}{(x_2 + x_1/2)(x_3 + x_1/2)} \quad (8)$$

such that for the binary system at composition  $x_i^\circ, x_j^\circ$

$$x_i - x_j = x_i^\circ - x_j^\circ \quad (9)$$

Tsao and Smith (5) proposed an equation for predicting the excess enthalpy of a ternary system. For excess molar volume, it is

$$V_{123}^E = \left( \frac{x_2}{1 - x_1} \right) V_{12}^E + \left( \frac{x_3}{1 - x_1} \right) V_{13}^E + (1 - x_1) V_{23}^E \quad (10)$$

in which the  $V_{ij}^E$  refer to the excess volume for the binary mixtures at compositions  $x_i^\circ, x_j^\circ$  such that  $x_i^\circ = x_i$  for the 1,2 and 1,3 binary systems and  $x_2^\circ = x_2/(x_2 + x_3)$  for the 2,3 binary system.

Singh et al. (6) proposed an equation of the following form:

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E + Ax_1 x_2 x_3 + Bx_1(x_2 - x_3) + Cx_1^2(x_2 - x_3)^2 \quad (11)$$

where  $A$ ,  $B$ , and  $C$  are parameters characteristic of the mixtures evaluated by fitting this equation by the method of least squares, with a standard deviation defined as eq 2.

The parameters obtained for this system for 298.15 K are  $A = 1.841 \times 10^{-7} \text{ m}^3 \text{mol}^{-1}$ ,  $B = -1.5296 \times 10^{-8} \text{ m}^3 \text{mol}^{-1}$ ,

**Table V. Standard Deviations for Molar Excess Volumes for the Tetrachloroethene (1) + 1,4-Dioxane (2) + Tetrahydrofuran (3) System at 298.15 and 308.15 K**

eq	$\sigma(V^E) \times 10^6 / (\text{m}^3 \text{mol}^{-1})$	
	298.15 K	308.15 K
4	8.6	7.1
6	7.2	6.9
7	7.9	5.7
8	6.7	5.3
10	7.5	7.2
11	8.7	6.4

and  $C = 5.37 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$  and for 308.15 K are  $A = 3.87 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$ ,  $B = -1.8482 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ , and  $C = -1.354 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}$ .

Table V shows the standard deviations calculated from applications of eq 4 of Rastogi, eq 6 of Radojkovič, eq 7 of Kohler, eq 8 of Jacob and Fitzner, eq 10 of Tsao and Smith, and eq 11 of Singh et al. for molar excess volumes for the ternary system at different temperatures.

Examination of Table V reveals that eq 8 of Jacob and Fitzner shows the best agreement with the experimental data.

Registry No.  $\text{Cl}_2\text{C}=\text{CCl}_2$ , 127-18-4; 1,4-dioxane, 123-91-1; tetrahydrofuran, 109-99-9.

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## Densities and Viscosities of 2-Butanone/Dibutyl Ether, 2-Picoline/2-Butanone, and 2-Picoline/Water Mixtures

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**Densities and viscosities of the binary mixtures including 2-butanone/dibutyl ether, 2-picoline/2-butanone, and 2-picoline/water are measured at 303.15, 313.15, and 323.15 K over the entire molar fraction range. The excess volumes, viscosities, and Gibbs energies of activation of flow are calculated from the experimental data, and are correlated by a Redlich-Kister-type function in terms of molar fraction. McAllister's three-body and four-body interaction models are also used to correlate the kinematic viscosities.**

### Introduction

Densities and viscosities of fluids and fluid mixtures are essential for engineering applications. The variations of these properties with temperature and composition for mixtures containing polar and/or hydrogen-bonding components may be complex due to strongly polar and/or hydrogen-bonding effects in the mixtures. In this work, three binary systems containing 2-butanone, dibutyl ether, 2-picoline, and water were investigated at atmospheric pressure (nominal value 0.1 MPa) and at 303.15, 313.15, and 323.15 K over the entire range of molar fraction.

### Experimental Section

Dibutyl ether (99+ wt %), 2-butanone (99.7+ wt %), methanol (99+ wt %), and toluene (99+ wt %) were purchased from Aldrich. Ethanol (99.8+ wt %, Ferak) and 2-picoline (98 wt %, Janssen) were also used in this work. Deionized distilled water (conductivity better than  $2 \times 10^{-6} \Omega^{-1}$

$\text{cm}^{-1}$ ) was prepared in our laboratory. All the substances were used without further purification.

Density was measured with three 25  $\text{cm}^3$  pycnometers (products of Kimax, Japan). The internal volumes of the pycnometers were calibrated with pure water (1) at each of the measured temperatures. All mixtures were prepared metrically with an accuracy better than  $\pm 0.5$  mg, and the nominal mass of the mixtures prepared was about 150 g. To minimize the errors in composition that arise from evaporation during the solution preparation, we charged the heavier component first. The loaded pycnometers were immersed in a thermostat (Neslab, RTE-220D) controlled within  $\pm 0.01$  K. The temperature readings were calibrated with a Hart Scientific Microtherm 1006 (accuracy  $\pm 0.02$  K) to  $\pm 0.1$  K. The readings from three pycnometers were averaged to determine the density. The accuracy of the reported densities was better than  $\pm 0.1\%$ . The change of composition due to evaporation during the measurement was minor according to the analysis by gas chromatography.

Viscosity was measured with a HAAKE falling-ball viscometer. The measuring tube was immersed in an insulated jacket wherein constant-temperature water (controlled within  $\pm 0.1$  K) was circulated. The temperature was measured by a platinum resistance temperature detector (RTD) probe with a DP86-R display (Omega product) calibrated to  $\pm 0.1$  K. The falling time ( $t$ , s) can be converted into dynamic viscosity ( $\eta$ , Pa s) by

$$\eta = K(\rho_b - \rho_m)t \quad (1)$$

where  $\rho_b$  is the density of the ball. In this work, a borosilicate glass ball with a density of  $2.219 \times 10^3 \text{ kg m}^{-3}$  was used for the full range of the experimental conditions. The notation of  $\rho_m$  refers to the density of the liquid determined at the measuring temperature, and  $K$  in eq 1 is the ball constant. To ensure the results are accurate to better than  $\pm 1\%$ , the ball constant

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