sured densities of less than $^1/_2$ of 1% would, however, bring the two sets of data into agreement. Much larger errors in the direct measurement of the volumes, as in the case of dilatometric measurements, can be tolerated without making such significant variations.

These results allow us to draw a qualitative conclusion concerning the dependence of excess molar entropy S^E on pressure. According to Maxwell's equation

$$(\partial S^E/\partial P)_T = -(\partial V^E/\partial T)_P \qquad (2)$$

and from the previous discussion, we get a positive derivative $(\partial S^E/\partial P)_T$, and the deviation from ideal behavior thus increases with pressure.

Glossary

A_k	curve-fitting parameters
P	pressure
S^E	excess entropy
T	temperature
V^E	excess volume
δV^E	deviation of measured excess volumes from correlation
x	mole fraction benzene

Registry No. Benzene, 71-43-2; trichloroethylene, 79-01-6.

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Received for review May 25, 1988. Accepted March 14, 1989.

Thermodynamic Properties of Some Organic Compounds with Tetrachloroterephthaloyl Oligomers by Gas Chromatography

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Specific retention volumes of 30 solutes in three stationary phases, *O,O″*-1,3-propanediyl *O′,O‴*-di-*n*-propyl bis(tetrachloroterephthalate) at 130, 140, and 150 °C, *O,O″*-1,3-propanediyl *O′,O‴*-di-*n*-butyl bis(tetrachloroterephthalate) at 110, 122, and 130 °C, and a propyl-trimer mixture at 110 and 130 °C, were determined by gas chromatography. Activity coefficients at infinite dilution and excess partial molar thermodynamic properties are reported at 130 °C. Relative retentions and selectivities for three series of meta and para isomers in the aforementioned liquid phases are discussed. Also, the variation of specific retention volume and activity coefficient with the liquid-phase molecular weight of a group of tetrachloroterephthalate esters is described.

Introduction

It has been shown in a previous work (*1*) that tetrachloroterephthalate esters are suitable as a stationary liquid phase in gas chromatography. The wide range of temperatures over which they can be used, the possibility of making derivative compounds taking the tetrachloroterephthaloyl nucleus as the basic unit (*2*, *3*), and their selectivity for the separation of aromatic isomers are some of the major features that make them a good choice for a liquid phase in gas chromatography.

Data of thermodynamic properties at 100 and 110 °C have been reported already (*1*) for four tetrachloroterephthalate esters (TCTP) (di-*n*-propyl-, di-*n*-butyl-, di-*n*-amyl-, and di-*n*-octyl-TCTP) with aromatic compounds as solvents.

To further explore the behavior of TCTP esters as liquid phases in chromatography, a study of thermodynamic properties of 30 solutes in higher molecular weight TCTP esters is reported in this work. The synthesis of the esters used as stationary phases has been reported (*2*). These include the compounds *O,O″*-1,3-propanediyl *O′,O‴*-di-*n*-propyl bis(tetrachloroterephthalate) (1,3-propanediyl(PrTCTP)$_2$), *O,O″*-1,3-propanediyl *O′,O‴*-di-*n*-butyl bis(tetrachloroterephthalate) (1,3-propanediyl(BuTCTP)$_2$), and bis(3-((4-(propoxycarbonyl)-2,3,5,6-tetrachlorobenzoyl)oxy)propyl) tetrachloroterephthalate. This last compound was not used in its pure form as the liquid phase because of its high melting point but was mixed with 1,3-propanediyl(PrTCTP)$_2$ in 59.6 wt % of this TCTP ester. This mixture will be referred to throughout this work as Pr-trimer mixture.

Experimental Section

The gas chromatograph used for this study is a modified Perkin-Elmer Model 800 gas chromatograph equipped with a thermal conductivity detector. Its modifications were described in a previous work (*1*). The column temperature could be controlled to ±0.02 °C and was measured with a precision thermometer inserted into the center of the oven.

The columns with 1,3-propanediyl(PrTCTP)$_2$ and Pr-trimer mixture were made of stainless steel tubing, 0.64 cm × 1.4 m, the liquid phases being supported on 60-80 mesh Gas Chrom RZ from Applied Science Laboratory, Inc. The amount of liquid phase in both columns was 15%. The column with 1,3-propanediyl(BuTCTP)$_2$ was prepared in the same way but was made of 0.48 cm × 2.40 m tubing and the amount of liquid phase was 8% of the dried coated support. The packed columns were conditioned under a gentle flow of helium for about 18 h at 100 °C.

Commercial solutes were used without any further purification, and mixtures containing between four and eight solutes were injected depending on the individual retention times of the

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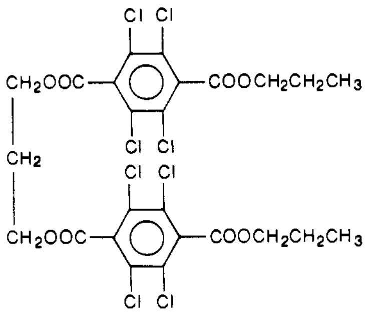
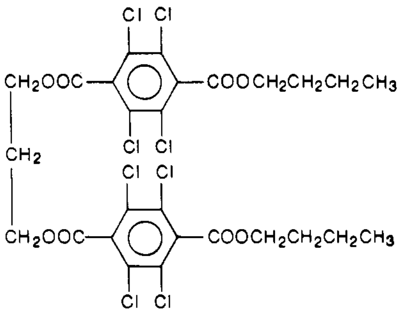


1,3-propanediyl(PrTCTP)$_2$



1,3-propanediyl(BuTCTP)$_2$

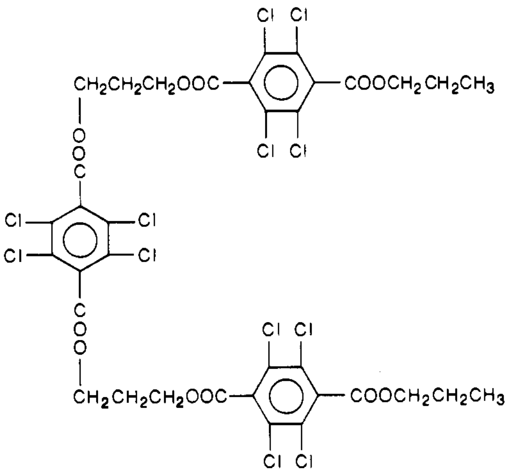


Table I. Specific Retention Volumes (V_g^T) of Solutes in TCTP Esters as Liquid Phases

solutes		1,3-propanediyl(PrTCTP)$_2$			1,3-propanediyl(BuTCTP)$_2$			trimer mixture	
no.		130 °C	140 °C	150 °C	110 °C	122 °C	130 °C	110 °C	130 °C
1	methylcyclohexane	22.8	18.8	15.8	39.3	29.3	26.2	33.9	22.6
2	octane	23.7	19.2	15.8	44.7	32.2	28.0	33.4	22.9
3	decane	79.2	60.2	46.5	177.9	122.5	96.7	135.6	76.0
4	benzene	31.2	25.8	20.8	51.1	39.1	32.8	49.8	32.0
5	toluene	58.0	46.0	36.9	103.6	75.9	62.0	99.0	59.5
6	ethylbenzene	92.9	72.3	56.8	178.1	124.1	100.3	164.0	94.3
7	propylbenzene	152.0	115.8	89.5	298.4	208.5	166.1	280.3	153.8
8	butylbenzene	273.7	203.1	153.0	592.9	390.0	303.3	535.3	276.6
9	*o*-xylene	132.5	101.2	78.6	257.0	178.8	142.4	244.4	135.5
10	*m*-xylene	101.3	78.1	61.2	195.3	137.0	110.1	182.6	103.1
11	*p*-xylene	106.2	81.7	63.8	204.4	143.5	114.2	193.3	108.5
12	1-methyl-2-ethylbenzene	197.2	148.6	112.5	402.5	271.9	213.3	372.9	199.3
13	1-methyl-2-ethylbenzene	155.5	118.0	89.9	314.3	214.7	171.0	287.7	155.9
14	1-methyl-4-ethylbenzene	166.3	125.2	95.1	336.3	229.2	180.5	310.4	166.7
15	1,2,3-trimethylbenzene	295.1	218.1	163.0	625.2	411.4	318.1	587.1	301.3
16	1,2,4-trimethylbenzene	244.4	167.5	126.6	470.0	313.1	243.6	438.1	227.8
17	1,3,5-trimethylbenzene	164.0	123.4	94.3	342.1	229.7	181.4	309.2	165.4
18	isopropylbenzene	125.2	95.6	74.2	243.6	168.9	135.5	223.9	124.7
19	*tert*-butylbenzene	183.9	138.9	106.5	387.1	254.6	202.4	342.4	183.8
20	styrene	152.8	116.5	89.8	297.5	206.1	163.3	288.6	157.7
21	anisole	189.3	142.4	108.3	381.9	255.6	198.2	370.6	196.2
22	fluorobenzene	33.7	27.3	22.2	56.5	42.8	35.3	55.7	34.7
23	chlorobenzene	117.9	91.2	71.4	218.9	155.1	125.2	212.8	121.6
24	bromobenzene	218.7	166.1	127.7	428.7	293.7	232.1	217.5	226.6
25	iodobenzene	467.2	346.5	260.1	972.6	643.0	497.4	942.4	485.4
26	*o*-chlorotoluene	231.0	159.5	122.2	423.0	288.9	225.8	406.4	218.1
27	*m*-chlorotoluene	218.3	164.3	125.4	439.9	298.7	233.7	420.4	235.3
28	*p*-chlorotoluene	233.5	174.5	132.5	467.8	316.7	247.3	451.3	239.4
29	2,6-dichlorotoluene	421.1	311.6	233.3	946.5	580.0	447.0	831.3	465.3
30	3,5-dichlorotoluene	331.3	246.2	145.6	805.9	454.2	315.8	659.6	345.4

solutes. Samples were kept small, usually between 0.1 and 0.2 μL, in order to avoid any possible sweeping of the liquid phase. No bleeding was noticeable for any of the liquid phases at the operating conditions mentioned above.

Results

The activity coefficients for the solutes at infinite dilution (γ_p^∞) were obtained from the expression:

$$\gamma_p^\infty = \frac{RT}{M_s V_g^T p^\circ} \tag{1}$$

The molecular weight for the trimer mixture was taken as the average of the two components (equal to 871). Solute activity coefficients were corrected for the nonideality of the vapor phase according to the equation:

$$\ln \gamma_f^\infty = \ln \frac{RT}{M_s V_g^T p^\circ} - \frac{p^\circ (B_{22} - V_2^\circ)}{RT} - \frac{p^\circ J}{RT}(2B_{23} - \bar{V}_2^\infty) \tag{2}$$

The partial molar excess thermodynamic functions for the solutes $\Delta\bar{G}_e^\infty$, $\Delta\bar{H}_e^\infty$, and $\Delta\bar{S}_e^\infty$ are easily obtained from γ_f^∞:

$$\ln \gamma_f^\infty = \frac{\Delta\bar{G}_e^\infty}{RT} = \frac{\Delta\bar{H}_e^\infty}{RT} - \frac{\Delta\bar{S}_e^\infty}{R} \tag{3}$$

The $\Delta\bar{H}_e^\infty/RT$ term is known as the thermal contribution to the activity coefficient (γ_T^∞) and gives a measure of the energetic interactions between the solvent and solute. The $\Delta\bar{S}_e^\infty/R$ term is known as the athermal contribution to the activity coefficient (γ_A^∞) and gives an indication of the differences in size and shape of the molecules. The athermal contribution can be split into two terms. One is related to the size difference between the solvent and solute (γ_{F-H}^∞), and the other includes all the other entropic contributions (γ_{I-S}^∞) (*4*). Thus:

$$\gamma_f^\infty = \gamma_T^\infty \gamma_A^\infty = \gamma_T^\infty \gamma_{F-H}^\infty \gamma_{I-S}^\infty \tag{4}$$

Values for the retention volume V_g^T at several temperatures are listed in Table I for each phase. The activity coefficient (γ_f^∞) at 130 °C and excess properties $\Delta\bar{H}_e^\infty$ and $\Delta\bar{S}_e^\infty$ are listed in Table II. The contributions to the activity coefficient

Table II. Activity Coefficients at 130 °C and Excess Partial Thermodynamic Properties of the Solutes at Infinite Dilution in TCTP Esters

solutes		1,3-propanediyl-(PrTCTP)$_2$			1,3-propanediyl(BuTCTP)$_2$			trimer mixture		
no.		γ_f^∞	$\Delta\bar{H}_e^\infty$	$\Delta\bar{S}_e^\infty$	γ_f^∞	$\Delta\bar{H}_e^\infty$	$\Delta\bar{S}_e^\infty$	γ_f^∞	$\Delta\bar{H}_e^\infty$	$\Delta\bar{S}_e^\infty$
1	methylcyclohexane	1.006	143	0.34	0.843	305	1.10	0.852	381	1.26
2	octane	1.805	540	0.17	1.470	479	0.42	1.569	1949	3.94
3	decane	2.094	405	−0.47	1.652	1300	2.23	1.836	907	1.04
4	benzene	0.424	−913	−0.56	0.388	−567	0.47	0.348	−581	0.66
5	toluene	0.491	−734	−0.41	0.442	−672	−0.05	0.402	−621	0.27
6	ethylbenzene	0.599	−521	−0.27	0.534	−736	−0.58	0.496	−405	0.39
7	propylbenzene	0.688	−359	−0.15	0.542	1509	4.96	0.511	1428	4.88
8	butylbenzene	0.767	−281	−0.17	0.667	−388	−0.16	0.639	−219	0.35
9	*o*-xylene	0.525	−726	−0.52	0.471	−658	−0.13	0.431	−644	0.08
10	*m*-xylene	0.595	−603	−0.46	0.528	−1444	−2.31	0.492	−1365	−1.97
11	*p*-xylene	0.556	−766	−0.73	0.498	−763	−0.51	0.478	−706	−0.20
12	1-methyl-2-ethylbenzene	0.632	−615	−0.61	0.563	−533	−0.18	0.525	−403	0.28
13	1-methyl-3-ethylbenzene	0.721	−518	−0.64	0.632	−283	0.21	0.605	−325	0.19
14	1-methyl-4-ethylbenzene	0.684	−727	−1.05	0.606	−502	−0.25	0.573	−494	−0.12
15	1,2,3-trimethylbenzene	0.579	−632	−0.48	0.517	−734	−0.51	0.476	−593	0.01
16	1,2,4-trimethylbenzene	0.576	−2064	−4.02	0.557	−694	−0.56	0.520	−641	−0.29
17	1,3,5-trimethylbenzene	0.758	−392	−0.42	0.660	−452	−0.29	0.632	−308	0.15
18	isopropylbenzene	0.692	−511	−0.54	0.616	−351	0.09	0.584	−327	0.26
19	*tert*-butylbenzene	0.741	−310	−0.19	0.655	−729	−0.97	0.630	−270	0.25
20	styrene	0.465	−662	−0.12	0.419	−624	0.18	0.378	−698	0.20
21	anisole	0.484	−696	−0.28	0.445	1856	6.21	0.392	−765	−0.04
22	fluorobenzene	0.432	−822	−0.37	0.397	−647	0.23	0.353	−696	0.35
23	chlorobenzene	0.417	−879	−0.44	0.378	−699	0.20	0.340	−709	0.39
24	bromobenzene	0.431	−695	−0.05	0.392	−721	0.08	0.350	−676	0.41
25	iodobenzene	0.499	−362	0.48	0.452	−418	0.54	0.404	−309	1.04
26	*o*-chlorotoluene	0.448	−2333	−3.95	0.442	−757	−0.25	0.399	−685	0.13
27	*m*-chlorotoluene	0.528	−703	−0.47	0.475	−764	−0.42	0.412	31	1.84
28	*p*-chlorotoluene	0.486	−914	−0.83	0.442	−843	−0.47	0.398	−796	−0.15
29	2,6-dichlorobenzene	0.452	−575	0.15	0.410	−1818	−2.74	0.344	852	4.24
30	3,5-dichlorobenzene	0.460	−478	−0.31	0.465	−4902	−10.84	0.370	−537	0.64

have also been calculated but are not listed here as they may be readily generated from the reported data.

The consistency of experimental data was checked by plotting ln V_g^T vs $1/T$, for the two phases 1,3-propanediyl-(PrTCTP)$_2$ and 1,3-propanediyl(BuTCTP)$_2$ at three temperatures. The plots were linear with regression coefficients higher than 0.99, except for some high boiling solutes, such as *m*- and *p*-chlorotoluene and *o*- and *m*-dichlorobenzene, which showed slight deviations.

It has been stated that, in comparing two phases, a plot of the logarithms of V_g^T for several solutes in one liquid phase against the corresponding values in the second liquid phase should be linear if the interactions between solutes and liquid phases are similar (*1*). This was actually the case when a plot was made for 1,3-propanediyl(PrTCTP)$_2$ and 1,3-propanediyl-(BuTCTP)$_2$. The same plot for 1,3-propanediyl(BuTCTP)$_2$ and the Pr-trimer mixture in Figure 1 shows two straight-line correlations, one for the aliphatic and cycloalkane compounds and another for the aromatic compounds. The nature of aromatic and aliphatic compound interactions with TCTP esters has been discussed previously (*1*).

The slopes of the straight lines in Figure 1 are close to unity. This indicates the absence of marked preferential solute–solvent interaction.

The activity coefficients for the solutes show large negative deviations from Raoult's law for the aromatic compounds and positive deviations for the aliphatic compounds. Methylcyclohexane shows the closest values to unity. This result agrees with the behavior observed in previous works (*5*). There is no substantial variation of γ_f^∞ with temperature, which is usually found in systems in which the athermal contribution to the activity coefficient, γ_A^∞, predominates (*6*). Determination of γ_A^∞ and γ_T^∞ for the systems studied in this work indicates that $\gamma_A^\infty \gg \gamma_T^\infty$.

A comparison of the activity coefficients for some of the homologous series of solutes show a decreasing order as follows: γ_f^∞(methylethylbenzenes) > γ_f^∞(xylenes) > γ_f^∞(chlorotoluenes). The values of γ_f^∞ for the dichlorobenzenes show negligible differences from those obtained for chlorotoluenes.

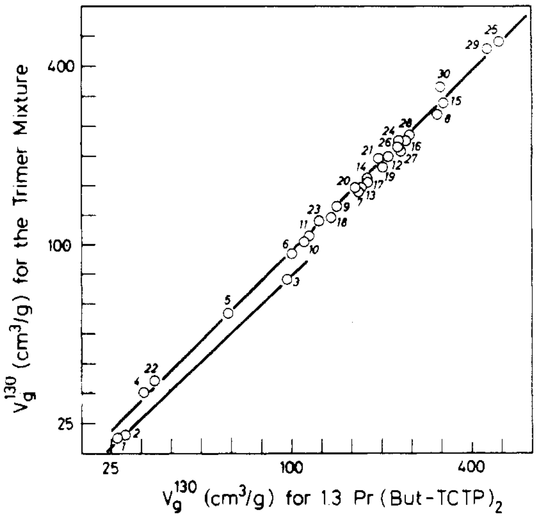


Figure 1. Log–log plot of V_g^T for solutes of Table I eluted from 1,3-propanediyl(BuTCTP)$_2$ and the trimer mixture at 130 °C.

The relative retention of two solutes in a liquid phase is defined as

$$\alpha_{21} = \frac{V_{g\,2}^T}{V_{g\,1}^T} = \frac{\gamma_p^\infty{}_1 p_1^\circ}{\gamma_p^\infty{}_2 p_2^\circ} \qquad (5)$$

α_{21} values give an indication of the efficiency of a stationary phase for the separation of two solutes. It is a parameter similar to the relative volatility in distillation α_R, and hence, infinite dilution coefficients obtained by chromatography provide information for the separation of close boiling temperature solutes by extractive distillation. Table III gives values of α_R and α_{21} for the meta/para isomers considered in this work. Selectivities for the aforementioned isomers defined as $S_{21} = \gamma_p^\infty/\gamma_p^\infty{}_2$ vary

Table III. Separation Factors of Meta/Para Isomers on TCTP Liquid Phases at 130 °C

		$\sigma_{21} = V_g^T(\text{para})/V_g^T(\text{meta})$		
isomers	σ_R- (para/meta)	1,3-propanediyl-$(\text{PrTCTP})_2$	1,3-propanediyl-$(\text{BuTCTP})_2$	trimer mixture
xylenes	0.974	1.047	1.040	1.052
methylbenzenes	1.015	1.069	1.056	1.069
chlorotoluenes	0.981	1.069	1.058	1.018

Table IV. Molecular Weights of Some TCP and TCTP Liquid Phases

liquid phase	M_s
(a) di-*n*-Pr-TCP	388
(b) di-*n*-Bu-TCTP	416
(c) di-*n*-amyl-TCTP	444
(d) di-*n*-octyl-TCTP	528
(e) 1,3-propanediyl$(\text{BuTCTP})_2$	760
(f) trimer mixture	871

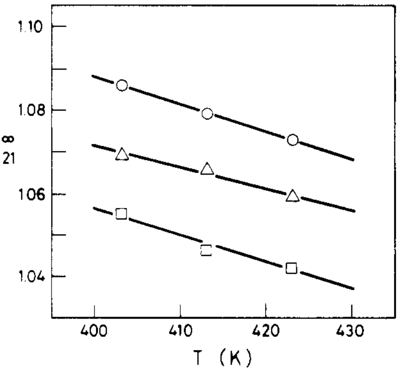


Figure 2. Selectivities in 1,3-propanediyl$(\text{PrTCTP})_2$ at 130 °C of meta/para isomers: ○, *m*-/*p*-xylenes; △, *m*-/*p*-methylethylbenzenes; □, *m*-/*p*-chlorotoluenes.

linearly with temperature as shown in Figure 2.

Plots of V_g^T or γ_f^{∞} for a series of solutes, i.e., aromatic compounds, as a function of the molecular weight of the TCTP liquid phase, M_s, follow a straight line. Besides the three liquid phases studied in this work, the liquid phases di-*n*-butyl-TCTP, di-*n*-amyl-TCTP, and di-*n*-octyl-TCTP reported previously (*1*) have also been considered in the V_g^T, γ_f^{∞} vs M_s plots. The molecular weights are indicated in Table IV.

The plot of V_g^T at 110 °C, for a group of solutes, as a function of M_s gives straight lines as shown in Figure 3. There are deviations for the lower molecular weight liquid phase di-*n*-propyl tetrachlorophthalate (di-*n*-Pr-TCP), but obviously this liquid phase does not belong to the TCTP series, and its polarity is higher than for the TCTP esters. For the other liquid phases the deviations from the linear behavior are small and V_g^T for a certain solute always decreases as M_s increases. Petsev and Dimitrov (*7*) reported, for a group of phthalic esters of lower molecular weight and a certain solute, that V_g^T increases as M_s increases. Hence, it can be concluded that V_g^T increases with M_s up to a certain value and that higher values of M_s lead to a decrease in V_g^T. This suggests that the variation of V_g^T with M_s can be described by a bell-shaped curve and that they vary linearly far away from the maximum value of M_s.

In addition, there is a relationship between the activity coefficients and the liquid-phase molecular weight. Activity coefficients γ_f^{∞} decrease linearly with M_s as shown in Figure 4. This is in agreement with the behavior observed by Petsev and Dimitrov (*7*).

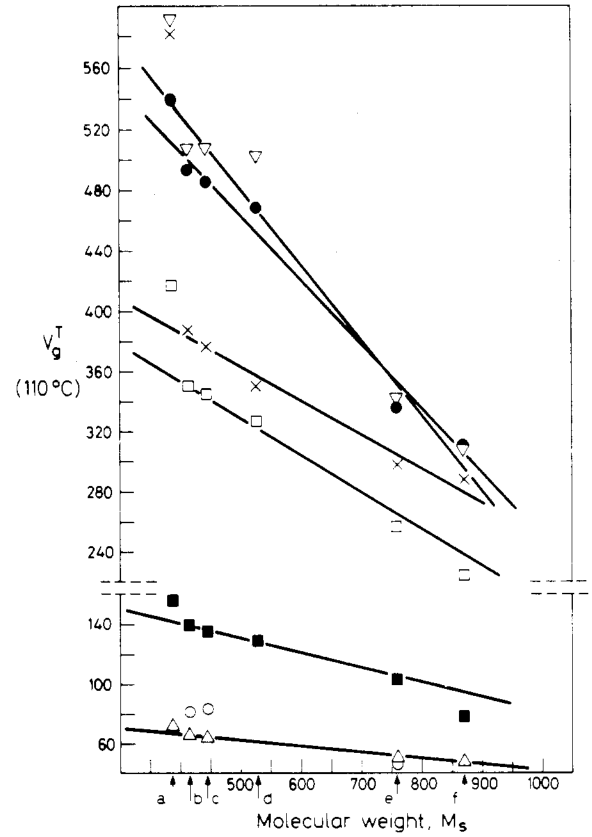


Figure 3. Plot of V_g^T of several hydrocarbons vs molecular weight, M_s, of esters in Table IV, at 110 °C. Hydrocarbons: ■, toluene; □, *o*-xylene; ×, styrene; ●, 1-methyl-4-ethylbenzene; ▽, 1,3,5-trimethylbenzene; △, benzene; ○, octane.

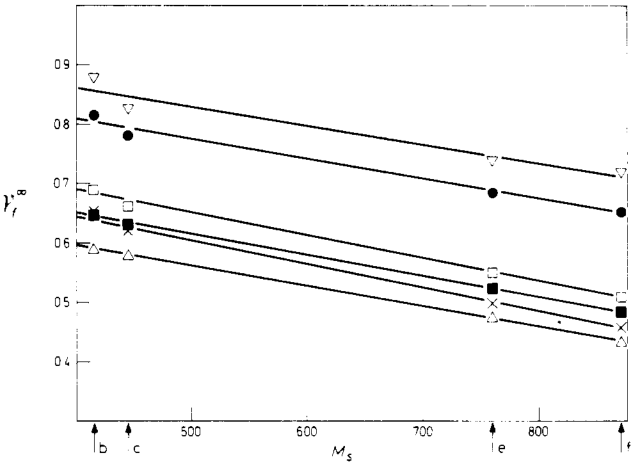


Figure 4. Plot of γ_f^{∞} of several hydrocarbons vs molecular weight, M_s, of esters in Table IV, at 110 °C. Hydrocarbons: ■, toluene; □, *o*-xylene; ×, styrene; ●, 1-methyl-4-ethylbenzene; ▽, 1,3,5-trimethylbenzene, △, benzene.

Glossary

B	virial coefficient, cm³/mol
$\Delta\bar{G}_e^{\infty}$	excess Gibbs free energy of mixing, cal/mol
$\Delta\bar{H}_e^{\infty}$	excess enthalpy of mixing, cal/mol
J	James-Martin compressibility factor
M_s	molecular weight of the stationary phase
p°	vapor pressure of the pure solute, mmHg
R	universal gas constant
T	temperature, K
S	selectivity
$\Delta\bar{S}_e^{\infty}$	excess entropy of mixing, cal/(mol·K)
V_2°	molar volume of solute, cm³/mol
$\bar{V}_2^{\infty}$	partial molar volume of the solute, cm³/mol
V_g^T	specific retention volume at column temperature, cm³/g of stationary phase
α	separation factor
α_R	relative volatility

γ_f^∞	corrected activity coefficient
γ_A^∞	athermal contribution to activity coefficient
γ_T^∞	thermal contribution to activity coefficient
γ_p^∞	activity coefficient
γ_{F-H}^∞	Flory–Huggins size effect correction
γ_{I-S}^∞	size-corrected athermal contribution

Registry No. 1, 108-87-2; **2**, 111-65-9; **3**, 124-18-5; **4**, 71-43-2; **5**, 108-88-3; **6**, 100-41-4; **7**, 103-65-1; **8**, 104-51-8; **9**, 95-47-6; **10**, 108-38-3; **11**, 106-42-3; **12**, 611-14-3; **13**, 620-14-4; **14**, 622-96-8; **15**, 526-73-8; **16**, 95-63-6; **17**, 108-67-8; **18**, 98-82-8; **19**, 98-06-6; **20**, 100-42-5; **21**, 100-66-3; **22**, 462-06-6; **23**, 108-90-7; **24**, 108-86-1; **25**, 591-50-4; **26**, 95-49-8; **27**, 108-41-8; **28**, 106-43-4; **29**, 118-69-4; **30**, 25186-47-4; 1,3-propanediyl-$(PrTCTP)_2$, 36640-96-7; 1,3-propanediyl-$(BuTCTP)_2$, 36640-93-4; bis(3-((4-propoxycarbonyl)-2,3,5,6-tetrachlorobenzoyl)oxy) tetrachloroterephthalate, 36640-98-9.

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Received for review October 7, 1988. Accepted January 13, 1989.

Liquid-Phase Enthalpy of Mixing for Binary Mixtures with Associated Components. The Mixture 1,3-Dioxolane–Acetic Acid

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The liquid-phase enthalpies of mixing for the system 1,3-dioxolane–acetic acid have been determined at 298.15, 306.15, and 313.15 K as a function of composition. Correlation of the calorimetric data was obtained by the Redlich–Kister empirical expression.

Introduction

The present work, an extension of our previous studies on binary mixtures of 1,3-dioxolane with associated components (*1*, *2*), deals with the calorimetric determination of the liquid-phase enthalpy of mixing (heat of mixing) for the system 1,3-dioxolane (D)–acetic acid (A). The aim of the present work is to determine and correlate the calorimetric data for the mixture D–A in the temperature range 298.15–313.15 K. The upper limit of 313.15 K is imposed by our LKB flow microcalorimeter; the lower limit of 298.15 K is due to the melting point of A (289.75 K).

Chemicals

1,3-Dioxolane (Fluka product, analytical grade 99%) was purified by refluxing for about 10 h on Na wires in N_2 flow, excluding moisture. It was then fractionated on a Vigreux column. For further details see also ref *3*. Acetic acid (C. Erba product, 99.8%) was used without purification: the major impurity is formic acid, 0.01%.

Liquid-Phase Enthalpy of Mixing: Calorimetric Measurements

The enthalpies of mixing ΔH for the mixture D–A were determined by a flow microcalorimeter Model 2107, LKB-Producter AB (Bremme, Sweden) described in ref *4*. Details of the calibration of the equipment and accuracy of measurements are given in ref *5*. Figure 1 and Table I gather the ΔH values as a function of the mole fraction of D. The calorimetric experiments were performed at 298.15, 306.15, and 313.15 ± 0.01 K (IPTS-68).

Table I. Values of the Experimental Enthalpies of Mixing ΔH for the System D–A as a Function of the Mole Fraction of D, at Three Temperatures

T = 298.15 K		T = 306.15 K		T = 313.15 K	
N_D	ΔH, J·mol^{-1}	N_D	ΔH, J·mol^{-1}	N_D	ΔH, J·mol^{-1}
0.0250	18.4	0.0249	18.6	0.0307	16.0
0.0330	24.7	0.0331	25.3	0.0405	22.0
0.0641	48.7	0.0641	48.2	0.0778	43.4
0.1205	87.9	0.1204	87.0	0.1204	72.8
0.1705	119.1	0.1704	113.2	0.1724	108.0
0.2151	144.8	0.2150	141.4	0.2149	132.2
0.2913	182.3	0.2912	176.3	0.2910	169.0
0.3539	207.4	0.3539	198.0	0.3537	192.5
0.4512	231.2	0.4510	225.5	0.4509	215.3
0.5522	237.5	0.5521	230.3	0.5519	222.4
0.6218	233.2	0.6217	225.9	0.6215	217.2
0.7115	213.2	0.7115	205.2	0.7196	200.6
0.7668	192.3	0.7667	185.8	0.7595	187.7
0.8315	161.4	0.8314	154.4	0.8313	154.9
0.8680	136.8	0.8679	132.2	0.8679	132.6
0.9080	103.3	0.9079	103.0	0.9079	102.6
0.9518	60.4	0.9517	60.4	0.9517	60.7
0.9634	48.7	0.9634	47.4	0.9633	47.1

Table II. Values of the Experimental Densities ρ_A of Acetic Acid as a Function of Temperature

T, K	ρ_A, kg·m^{-3}	T, K	ρ_A, kg·m^{-3}	T, K	ρ_A, kg·m^{-3}
290.70	1052.50	297.00	1045.45	307.25	1033.89
290.85	1052.45	299.65	1042.54	309.10	1031.82
291.10	1052.16	300.65	1041.35	310.30	1030.46
292.95	1049.94	304.65	1036.18	311.55	1029.04
293.65	1049.18	306.00	1035.33	313.15	1027.15

0021-9568/89/1734-0284$01.50/0