(55) Abraham, M. H.; Greller, P. L.; Mana, J. *J. Chem. Thermodyn.* **1974**, *6*, 1175.
(56) Maher, P. J.; Smith, B. D. *J. Chem. Eng. Data* **1980**, *25*, 61.
(57) Pul'tsin, M. N.; Galle, A. A.; Proskuryakov, V. A. *Russ. J. Phys. Chem. (Engl. Transl.)* **1973**, *47*, 428.
(58) Monfort, J. P.; Vidal, J.; Renon, H. *J. Chim. Phys. Phys.-Chim. Biol.* **1970**, *67*, 748.
(59) Pecsar, R. E.; Martin, J. J. *Anal. Chem.* **1966**, *38*, 1661.
(60) Karger, B. L.; Sewell, P. A.; Castells, R. C.; Hartkopf, A. *J. Colloid Interface Sci.* **1971**, *35*, 328.

Received for review June 29, 1981. Revised manuscript received May 26, 1982. Accepted June 18, 1982. We gratefully acknowledge the financial support provided by the National Science Foundation and Phillips Petroleum Co.

Vapor Pressures of Some C_4 Hydrocarbons and Their Mixtures

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New experimental vapor pressures for the six binary systems containing 1,3-butadiene, *n*-butane, *trans*-2-butene, and *cis*-2-butene at temperatures from 278 to 358 K are reported. Relative volatilities were calculated by using the isothermal general coexistence equation.

Recent investigators (*1*, *2*) have demonstrated the utility of the total pressure technique for obtaining vapor–liquid equilibrium information on systems of close-boiling components of sufficient accuracy to be used in distillation design. Laurance and Swift (*3*), Steele et al. (*4*), and Martinez-Ortiz and Manley (*5*), in particular, have presented vapor pressures for various combinations of the C_4 hydrocarbon isomers. This study is a continuation and extension of their work. Vapor pressures were measured for 1,3-butadiene, *n*-butane, *trans*-2-butene, *cis*-2-butene, and the six binary combinations of these four isomers. Temperature ranges were 278–338 K for butadiene and mixtures containing butadiene and 278–358 K for the remaining isomers and their mixtures.

Theory

The isothermal Gibbs–Duhem equation for a two-component system is

$$(V\,dP)/RT = z_1\,d\ln f_1 + z_2\,d\ln f_2 \qquad (1)$$

Writing this equation for both vapor and liquid phases and subtracting, noting that $f_i^V = f_i^L$ at equilibrium, gives

$$(1/RT)(V^V - V^L)\,dP = (y_1 - x_1)\,d\ln f_1 + (y_2 - x_2)\,d\ln f_2 \qquad (2)$$

or

$$(1/RT)(V^V - V^L)\,dP = (y_1 - x_1)\,d\ln (f_1/f_2) \qquad (3)$$

The fugacities are given by

$$f_i = y_i\phi_i P \qquad (4)$$

At this point it is necessary to decide upon an equation of state for the vapor phase in order to calculate the fugacity coefficient, ϕ_i. The virial equation truncated after the second term was judged to be sufficient for these systems. The Berlin form

$$Z = V^VP/RT = 1 + BP \qquad (5)$$

is somewhat more convenient to use than the Leiden form. The mixture virial coefficient, B, is taken to be

$$B = y_1B_1 + (1 - y_1)B_2 \qquad (6)$$

Using the commonly known relationship between fugacity and an equation of state

$$\phi_i = \exp(B_iP) \qquad (7)$$

It is further assumed that the liquid phase forms an ideal mixture

$$V^L = x_1V_1^L + (1 - x_1)V_2^L \qquad (8)$$

where V_i^L is the saturated-liquid volume. We are interested in calculating relative volatilities, so y_1 in the above equations will be replaced by α according to the relation

$$\alpha = y_1(1 - x_1)/[(1 - y_1)x_1] \qquad (9)$$

Combining eq 3–9 gives the result

$$\frac{(\alpha - 1)(1 - x)x}{1 + (\alpha - 1)x}\frac{d\ln\alpha}{dx} + \frac{\alpha - 1}{1 + (\alpha - 1)x} = A\frac{d\ln P}{dx} \qquad (10)$$

$$A = \mathrm{fcn}\,(x,P;V_1^L,B_i) \qquad (11)$$

where x is for the first component. Equation 10 is then integrated for α using the experimentally determined $P - x$ function.

Experimental Section

The equipment of Walker (*6*) and Steele (*7*) was used with only slight modifications to improve the reliability and speed. The primary element is an enclosed equilibrium cell immersed in a thermostated water bath. By means of a diaphragm mechanism, the pressure within the cell was balanced against an external nitrogen pressure which was then measured. The system was capable of handling up to four equilibrium cells at a time which significantly decreased the amount of time required to complete a binary. The temperature of the water bath was measured with a Leeds and Northrup platinum resistance thermometer calibrated by the National Bureau of Standards to the IPTS of 1968. Pressures at 278 K were measured with a Mensor Corp. quartz manometer, and those at the upper temperature with a Ruska Corp. dead-weight gauge with calibration traceable to NBS.

Phillips research-grade hydrocarbons were used which had stated purities of not less than 99.95, 99.95, 99.80, and 99.97 wt % for butadiene, *n*-butane, *trans*-2-butene, and *cis*-2-butene, respectively. Noncondensables were removed by a freezing and evacuating cycle. Analysis of the vapor phase by gas chromatograph showed no detectable noncondensable. The chromatograph was capable of detecting air mole fractions

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* This paper was presented at the 72nd Annual Meeting of the American Institute of Chemical Engineers, Nov 25–29, 1979, San Francisco, CA.

0021-9568/82/1727-0405$01.25/0

Table I. Experimental Vapor Pressures

	P, MPa			
T, K	1,3-butadiene	n-butane	*trans*-2-butene	*cis*-2-butene
278.15	0.144 72	0.124 56	0.118 13	0.106 63
	0.144 70	0.124 51	0.118 28	0.106 50
				0.106 65
298.15	0.281 65	0.243 68	0.233 74	0.213 91
	0.281 51	0.243 57	0.233 89	0.213 88
				0.214 05
318.15	0.499 68	0.434 30	0.421 19	0.389 63
	0.499 25	0.434 55	0.421 36	0.389 37
		0.434 61		0.389 61
338.15	0.824 25	0.720 66	0.704 33	0.656 76
	0.823 81	0.720 38	0.704 51	0.656 81
		0.720 72		
358.15		1.126 57	1.109 09	1.039 66
		1.126 07	1.109 18	1.039 32

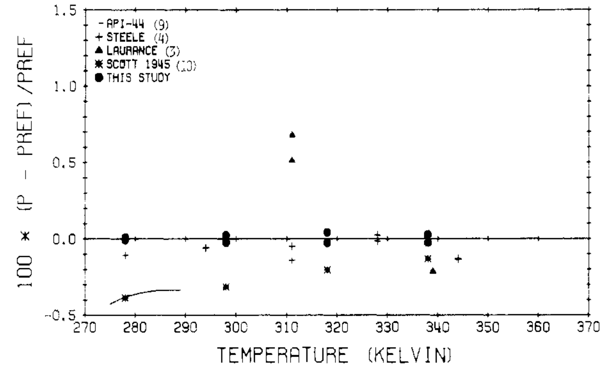

Figure 1. 1,3-Butadiene vapor pressures.

as low as 50 ppm. The mixtures were made by metering the components into the cell individually and weighing the cell after each addition on a Mettler analytical balance.

Each series of measurements on a sample was begun at the lowest temperature, 278 K. The temperature was increased by 20 K increments to the highest temperature and then decreased by the same increments. This gave a duplicate point at each temperature and served as a check on any possible reactions. An initial set of measurements on butadiene and two mixtures containing butadiene showed approximately 0.8% polymerization occurring at 358 K. These data were discarded, and subsequent measurements on butadiene systems were limited to 338 K. Because of the relatively short time that the samples were held at elevated temperatures, little polymerization occurred and no significant pressure drops were then observed.

Results

The experimental vapor pressures corrected to constant isotherms for the four pure components are given in Table I. These pressures were correlated by an equation given by Godwin (*8*)

$$\ln (P/P_R) = AX + BX^2 + CX^3 + DX(1 - X)^{3/2} \quad (12)$$

$$X = (1 - T_R/T)/(1 - T_R/T_C) \quad (13)$$

Here, P_R and T_R are a reference pressure and a reference temperature, taken as atmospheric pressure and the normal boiling point. Table II gives the constants for each component. The critical temperatures, T_C, are from API Project 44 (*9*). Figures 1–4 show the deviations of various literature values from this line. Differences in these pressures are probably the result of variations in the degassing technique and the amount of impurities in the samples. In general, noncondensables in the vapor phase result in pressures which are high by a constant amount, while heavy impurities in the liquid phase lower the pressure by a constant percentage.

Table II. Goodwin Constants for Pure Components

	1,3-butadiene	n-butane	*trans*-2-butene	*cis*-2-butene
A	−0.12665	4.2761	3.2093	4.33311
B	5.9138	−1.0720	0.68987	−0.94975
C	−1.8703	0.36754	−0.22929	0.27924
D	3.94262	−0.55279	0.54896	−0.48785
T_R, K	268.58	272.60	274.03	276.81
T_C, K	425.0	425.2	428.6	435.6

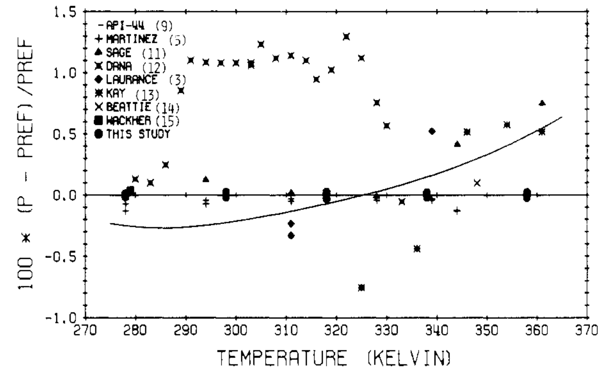

Figure 2. *n*-Butane vapor pressures.

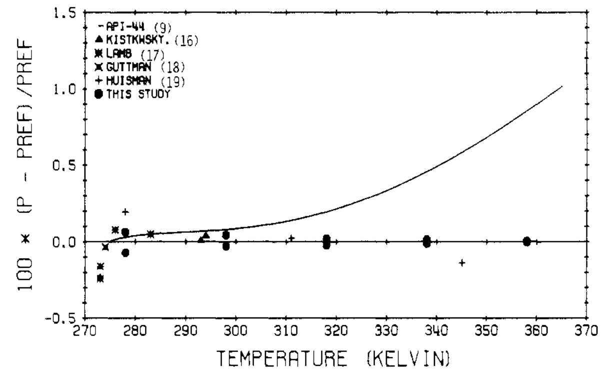

Figure 3. *trans*-2-Butene vapor pressures.

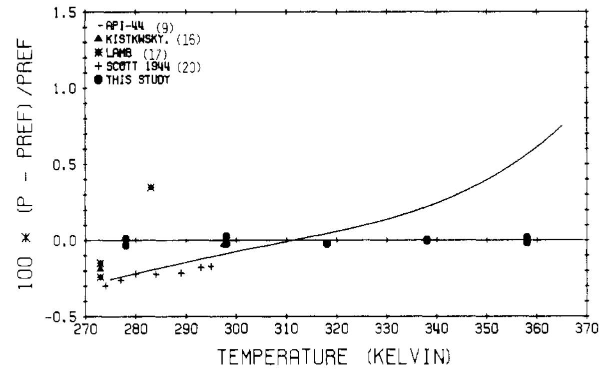

Figure 4. *cis*-2-Butene vapor pressures.

Table III contains the experimental vapor pressures for the six binaries corrected to constant isotherms.

The estimated probable error in the temperature measurements is ±0.007 K and that in the pressure measurements is ±100 Pa or 0.015%, whichever is larger. The liquid mole fraction was determined from the overall composition by assuming an ideal (Roault's law) mixture. The largest correction from overall mole fraction to liquid mole fraction was 0.0005

Table III. Experimental Vapor Pressure of Binaries

1,3-butadiene/*n*-butane

T, K	x	P, MPa	
278.15	0.0945	0.129 81	0.129 88
	0.2382	0.135 46	0.135 54
	0.5091	0.142 73	0.142 80
	0.7463	0.145 87	0.145 85
	0.8502	0.145 90	0.145 72
298.15	0.0945	0.252 31	0.252 40
	0.2381	0.262 63	0.262 70
	0.5091	0.276 04	0.276 12
	0.7462	0.282 48	0.282 42
	0.8502	0.282 75	0.282 60
318.15	0.0945	0.448 99	0.448 92
	0.2381	0.465 34	0.465 39
	0.5090	0.487 99	0.487 91
	0.7462	0.499 15	0.499 02
	0.8502	0.500 20	0.500 12
338.15	0.0944	0.741 66	0.741 69
	0.2380	0.766 99	0.767 04
	0.5089	0.802 54	0.802 57
	0.7461	0.820 72	0.820 70
	0.8502	0.823 37	0.823 14

1,3-butadiene/*trans*-2-butene

T, K	x	P, MPa	
278.15	0.0529	0.120 19	
	0.2657	0.126 30	0.126 32
	0.7516	0.139 25	0.139 29
	0.9048	0.142 68	0.142 80
	0.9515	0.143 75	0.143 67
298.15	0.0529	0.237 00	0.237 18
	0.2656	0.248 14	0.248 07
	0.7515	0.272 00	0.271 79
	0.9047	0.278 10	0.277 98
	0.9515	0.279 71	0.279 55
318.15	0.0529	0.426 41	0.426 38
	0.2655	0.444 46	0.444 28
	0.7515	0.483 96	0.483 77
	0.9047	0.493 78	0.493 46
	0.9515	0.496 46	0.496 12
338.15	0.0529	0.712 16	0.712 04
	0.2655	0.739 54	0.739 53
	0.7514	0.799 80	0.799 41
	0.9047	0.815 19	0.814 84
	0.9515	0.819 29	0.818 57

1,3-butadiene/*cis*-2-butene

T, K	x	P, MPa	
278.15	0.0882	0.110 31	0.110 46
	0.2503	0.116 82	0.116 82
	0.5029	0.126 41	0.126 50
	0.7498	0.135 66	0.135 80
298.15	0.0882	0.220 34	0.220 58
	0.2501	0.231 66	0.231 79
	0.5028	0.248 96	0.249 01
	0.7497	0.265 00	0.265 26
318.15	0.0882	0.400 03	0.400 08
	0.2500	0.418 48	0.418 51
	0.5027	0.446 44	0.446 17
	0.7496	0.472 80	0.472 71
338.15	0.0882	0.672 50	0.672 54
	0.2498	0.700 15	0.700 32
	0.5026	0.743 01	0.743 06
	0.7495	0.782 64	0.782 50

n-butane/*trans*-2-butene

T, K	x	P, MPa	
278.15	0.2488	0.121 55	0.121 71
	0.5019	0.123 59	0.123 27
	0.7493	0.124 22	0.124 23
	0.9001	0.124 57	
298.15	0.2488	0.239 55	0.239 74
	0.5019	0.242 56	0.242 41
	0.7493	0.243 39	0.243 66
	0.9001	0.243 35	0.243 57
318.15	0.2488	0.429 55	0.429 58
	0.5019	0.433 83	0.433 60
	0.7493	0.434 95	0.435 17
	0.9001	0.434 82	0.435 00
338.15	0.2488	0.715 93	0.715 86
	0.5019	0.721 32	0.720 80
	0.7493	0.721 74	0.721 96
	0.9001	0.721 29	0.721 49
358.15	0.2488	1.124 27	1.123 37
	0.7493	1.129 84	1.129 88
	0.9001	1.128 37	1.128 42

n-butane/*cis*-2-butene

T, K	x	P, MPa	
278.15	0.2642	0.113 69	0.113 80
	0.5000	0.118 51	0.118 61
	0.7507	0.121 47	
	0.8937	0.123 31	0.123 39
298.15	0.2642	0.225 61	0.225 83
	0.5000	0.233 35	0.233 67
	0.7506	0.238 62	0.238 55
	0.8937	0.241 72	0.241 76
318.15	0.2642	0.406 75	0.407 40
	0.5000	0.417 91	0.419 40
	0.7506	0.427 04	0.426 96
	0.8937	0.431 56	0.432 14
338.15	0.2642	0.681 90	0.681 99
	0.5000	0.698 88	0.698 98
	0.7506	0.710 08	0.710 01
	0.8937	0.716 67	0.717 34
358.15	0.2642	1.074 22	1.074 15
	0.5000	1.096 98	1.097 07
	0.7506	1.112 68	1.112 31
	0.8937	1.121 10	1.121 09

trans-2-butene/*cis*-2-butene

T, K	x	P, MPa	
278.15	0.2756	0.109 82	0.109 90
	0.5092	0.112 67	0.112 74
	0.7540	0.115 44	0.115 51
	0.8870	0.117 06	0.117 19
298.15	0.2756	0.219 44	0.219 49
	0.5091	0.224 32	0.224 36
	0.7540	0.229 12	0.229 14
	0.8870	0.231 67	0.231 83
318.15	0.2755	0.398 10	0.398 25
	0.5091	0.406 01	0.406 06
	0.7540	0.413 64	0.413 78
	0.8870	0.417 82	0.418 02
338.15	0.2755	0.669 65	0.669 78
	0.5090	0.681 29	0.681 26
	0.7540	0.693 16	0.692 83
	0.8870	0.699 06	0.699 34
358.15	0.2755	1.058 83	1.058 93
	0.5090	1.075 60	1.075 67
	0.8870	1.100 93	1.100 90

Table IV. Calculated Results for 1,3-Butadiene/*n*-Butane

	$T = 278.15$ K		$T = 298.15$ K		$T = 318.15$ K		$T = 338.15$ K	
x	α	P, MPa	α	P, MPa	α	P, MPa	α	P, MPa
0.0	1.452	0.124 54	1.380	0.243 63	1.321	0.434 49	1.269	0.720 58
0.1	1.380	0.129 89	1.324	0.252 78	1.277	0.449 01	1.234	0.742 40
0.2	1.312	0.134 20	1.272	0.260 35	1.236	0.461 29	1.201	0.761 10
0.3	1.251	0.137 65	1.225	0.266 59	1.198	0.471 61	1.171	0.777 03
0.4	1.197	0.140 40	1.181	0.271 70	1.163	0.480 23	1.142	0.790 50
0.5	1.150	0.142 57	1.142	0.275 83	1.130	0.487 32	1.115	0.801 70
0.6	1.108	0.144 22	1.106	0.279 08	1.099	0.492 98	1.089	0.810 77
0.7	1.065	0.145 37	1.069	0.281 41	1.068	0.497 19	1.064	0.817 71
0.8	1.017	0.145 94	1.028	0.282 75	1.034	0.499 85	1.037	0.822 41
0.9	0.962	0.145 79	0.982	0.282 90	0.998	0.500 72	1.009	0.824 63
1.0	0.904	0.144 71	0.934	0.281 57	0.959	0.499 46	0.979	0.824 03

Table V. Calculated Results for 1,3-Butadiene/*trans*-2-Butene

	$T = 278.15$ K		$T = 298.15$ K		$T = 318.15$ K		$T = 338.15$ K	
x	α	P, MPa	α	P, MPa	α	P, MPa	α	P, MPa
0.0	1.254	0.118 20	1.220	0.233 81	1.187	0.421 28	1.156	0.704 42
0.1	1.249	0.121 33	1.216	0.239 37	1.185	0.430 20	1.156	0.717 75
0.2	1.242	0.124 38	1.212	0.244 82	1.182	0.439 03	1.154	0.731 08
0.3	1.235	0.127 33	1.206	0.250 14	1.178	0.447 72	1.152	0.744 30
0.4	1.226	0.130 19	1.200	0.255 30	1.173	0.456 20	1.148	0.757 31
0.5	1.217	0.132 94	1.192	0.260 29	1.167	0.464 43	1.143	0.769 99
0.6	1.206	0.135 56	1.182	0.265 07	1.159	0.472 34	1.137	0.782 22
0.7	1.194	0.138 06	1.172	0.269 62	1.149	0.479 86	1.129	0.793 87
0.8	1.181	0.140 43	1.159	0.273 90	1.138	0.486 93	1.118	0.804 81
0.9	1.166	0.142 65	1.145	0.277 90	1.124	0.493 49	1.106	0.814 91
1.0	1.150	0.144 71	1.129	0.281 57	1.109	0.499 46	1.092	0.824 03

Table VI. Calculated Results for 1,3-Butadiene/*cis*-2-Butene

	$T = 278.15$ K		$T = 298.15$ K		$T = 318.15$ K		$T = 338.15$ K	
x	α	P, MPa	α	P, MPa	α	P, MPa	α	P, MPa
0.0	1.377	0.106 59	1.320	0.213 92	1.274	0.389 59	1.236	0.656 79
0.1	1.368	0.110 75	1.313	0.221 23	1.267	0.401 35	1.229	0.674 60
0.2	1.359	0.114 80	1.305	0.228 35	1.261	0.412 85	1.223	0.692 00
0.3	1.350	0.118 76	1.298	0.235 32	1.254	0.424 10	1.216	0.709 05
0.4	1.341	0.122 62	1.291	0.242 15	1.248	0.435 15	1.211	0.725 79
0.5	1.333	0.126 40	1.284	0.248 85	1.242	0.446 02	1.205	0.742 29
0.6	1.326	0.130 11	1.279	0.255 46	1.237	0.456 76	1.201	0.758 62
0.7	1.320	0.133 78	1.274	0.262 01	1.234	0.467 42	1.198	0.774 87
0.8	1.315	0.137 42	1.271	0.268 51	1.231	0.478 05	1.196	0.791 13
0.9	1.314	0.141 06	1.270	0.275 02	1.230	0.488 71	1.195	0.807 48
1.0	1.317	0.144 71	1.272	0.281 57	1.232	0.499 46	1.196	0.824 03

Table VII. Calculated Results for *n*-Butane/*trans*-2-Butene

	$T = 278.15$ K		$T = 298.15$ K		$T = 318.15$ K		$T = 338.15$ K		$T = 358.15$ K	
x	α	P, MPa	α	P, MPa	α	P, MPa	α	P, MPa	α	P, MPa
0.0	1.143	0.118 20	1.116	0.233 81	1.091	0.421 28	1.070	0.704 42	1.051	1.109 14
0.1	1.119	0.119 82	1.096	0.236 49	1.075	0.425 23	1.057	0.709 83	1.041	1.115 96
0.2	1.097	0.121 14	1.077	0.238 64	1.058	0.428 39	1.045	0.714 12	1.032	1.121 36
0.3	1.076	0.122 18	1.059	0.240 32	1.044	0.430 81	1.033	0.717 39	1.023	1.125 44
0.4	1.056	0.122 98	1.043	0.241 58	1.031	0.432 59	1.023	0.719 73	1.015	1.128 29
0.5	1.040	0.123 57	1.029	0.242 47	1.020	0.433 80	1.014	0.721 26	1.008	1.130 05
0.6	1.026	0.123 97	1.018	0.243 07	1.011	0.434 53	1.006	0.722 08	1.002	1.130 81
0.7	1.016	0.124 24	1.010	0.243 41	1.004	0.434 87	1.000	0.722 31	0.997	1.130 69
0.8	1.009	0.124 40	1.004	0.243 58	0.999	0.434 92	0.995	0.722 06	0.992	1.129 83
0.9	1.005	0.124 48	1.000	0.243 63	0.995	0.434 76	0.991	0.721 44	0.988	1.128 33
1.0	1.004	0.124 54	1.000	0.243 63	0.994	0.434 49	0.989	0.720 58	0.986	1.126 32

unit and the probable error in x is ±0.0001 unit.

Relative Volatilities

Equation 10 was integrated for each of the six binaries by using a point relaxation technique. The results are presented in Tables IV–IX. Table X contains the constants and equations used to calculate the saturated-liquid volumes and virial coefficients used in the integration. The constants and equations for liquid volume were derived from those given by API (*21*). Virial coefficients were taken from literature values and fitted with a polynomial equation. Sources were as follows: for butadiene, Meyers et al. (*22*); for butane, Sage et al. (*11*), Kay (*13*), Olds et al. (*23*), and Sliwinski (*24*); for *trans*-2-butene, Roper (*25*), and Huisman and Sage (*19*); for *cis*-2-butene, Roper (*25*). Extrapolation from 343 to 358 K for *cis*-2-butene was necessary because of the limited data. The estimated accuracy of the polynomial fit to temperature is 5% for butadiene and butane and 10% for *trans*-2-butene and *cis*-2-butene.

Table VIII. Calculated Results for *n*-Butane/*cis*-2-Butene

	$T = 278.15$ K		$T = 298.15$ K		$T = 318.15$ K		$T = 338.15$ K		$T = 358.15$ K	
x	α	P, MPa	α	P, MPa	α	P, MPa	α	P MPa	α	P, MPa
0.0	1.295	0.106 59	1.228	0.213 92	1.180	0.389 59	1.146	0.656 79	1.120	1.039 49
0.1	1.263	0.109 68	1.205	0.218 88	1.162	0.396 98	1.130	0.667 34	1.106	1.054 24
0.2	1.231	0.112 37	1.181	0.223 24	1.144	0.403 52	1.115	0.676 68	1.092	1.067 15
0.3	1.199	0.114 69	1.158	0.227 05	1.126	0.409 28	1.100	0.684 88	1.079	1.078 39
0.4	1.169	0.116 67	1.136	0.230 36	1.109	0.414 32	1.087	0.692 06	1.068	1.088 13
0.5	1.142	0.118 37	1.117	0.233 24	1.092	0.418 73	1.075	0.698 32	1.058	1.096 57
0.6	1.121	0.119 83	1.101	0.235 75	1.082	0.422 58	1.065	0.703 80	1.049	1.103 91
0.7	1.105	0.121 12	1.088	0.237 96	1.071	0.425 99	1.056	0.708 62	1.043	1.110 35
0.8	1.095	0.122 29	1.079	0.239 96	1.064	0.429 04	1.050	0.712 93	1.038	1.116 12
0.9	1.093	0.123 41	1.074	0.241 82	1.059	0.431 83	1.046	0.716 87	1.036	1.121 46
1.0	1.097	0.124 54	1.074	0.243 63	1.056	0.434 49	1.044	0.720 58	1.035	1.126 58

Table IX. Calculated Results for *trans*-2-Butene/*cis*-2-Butene

	$T = 278.15$ K		$T = 298.15$ K		$T = 318.15$ K		$T = 338.15$ K		$T = 358.15$ K	
x	α	P, MPa	α	P, MPa	α	P, MPa	α	P, MPa	α	P, MPa
0.0	1.109	0.106 59	1.090	0.213 92	1.075	0.389 59	1.064	0.656 79	1.054	1.039 49
0.1	1.108	0.107 81	1.089	0.215 99	1.075	0.392 85	1.063	0.661 64	1.053	1.046 51
0.2	1.107	0.109 01	1.088	0.218 04	1.074	0.396 09	1.063	0.666 48	1.053	1.053 52
0.3	1.106	0.110 20	1.087	0.220 07	1.073	0.399 32	1.062	0.671 30	1.052	1.060 52
0.4	1.105	0.111 38	1.087	0.222 09	1.072	0.402 52	1.061	0.676 09	1.052	1.067 50
0.5	1.104	0.112 55	1.086	0.224 09	1.071	0.405 70	1.061	0.680 87	1.051	1.074 47
0.6	1.102	0.113 70	1.085	0.226 07	1.071	0.408 86	1.060	0.685 62	1.051	1.081 43
0.7	1.101	0.114 85	1.084	0.228 03	1.070	0.412 00	1.060	0.690 36	1.050	1.088 38
0.8	1.100	0.115 98	1.083	0.229 98	1.070	0.415 11	1.059	0.695 07	1.050	1.095 31
0.9	1.098	0.117 10	1.082	0.231 91	1.069	0.418 21	1.058	0.699 76	1.049	1.102 23
1.0	1.097	0.118 20	1.081	0.233 81	1.068	0.421 28	1.058	0.704 42	1.048	1.109 14

Table X. Constants for Liquid Volumes and Second Virial Coefficients

	1,3-butadiene	*n*-butane	*trans*-2-butene	*cis*-2-butene
a	17.7256	15.0324	16.2977	16.5419
b	0.01865	0.01487	0.01636	0.01604
c	129.4	120.4	124.8	124.8
d	459.2	459.2	464.2	462.3
a'	3.6296	19.0437	3.8344	4.5900
b'	-2.4427×10^{-2}	-16.2074×10^{-2}	-2.0086×10^{-2}	-2.4378×10^{-2}
c'	5.8301×10^{-5}	4.6642×10^{-4}	2.7713×10^{-5}	3.3522×10^{-5}
d'	-4.7588×10^{-8}	-4.4919×10^{-7}	0.0	0.0

$V^{L} = (a - bT - c/(d - T))^{-1}$

$-B = a' + b'T + c'T^2 + d'T^3$

The pressures were correlated with a form of Redlich–Kister equation

$$\ln (P/P_R) = x(1 - x)(B + C(2x - 1) + D(2x - 1)^2) \tag{14}$$

The reference pressure, P_R, is the Raoult's law pressure

$$P_R = xP_1 + (1 - x)P_2 \tag{15}$$

where the pure-component vapor pressures are averaged from the experimental data.

Figures 5 and 6 show eq 14, along with the experimental points, for two binaries, chosen as representative. For each binary, a least-squares fit of the isothermal experimental data was made to eq 14. The constants were then smoothed with temperature. Constants for each binary and isotherm are given in Table XI. The number of constants varied with the quality of fit required—three were deemed necessary for the butadiene/butane binary, and one sufficient for the *trans*-2-butene/*cis*-2-butene binary. The B constant indicates the size of the deviation from Raoult's law, and the C constant accounts for the skew in the curve.

The calculation of the relative volatilities is most sensitive to errors in the deviation from Raoult's law. Secondary sources of uncertainties are errors in the pure-component vapor pressures and the virial coefficients. Errors in the liquid volume have negligible effect. For the constants used in these calculations (Tables II, X, and XI) the estimated probable errors in the relative volatilities for each binary are as follows: butadiene/*n*-butane, ±0.005; butadiene/*trans*-2-butene, ±0.010; butadiene/*cis*-2-butene, ±0.010; *n*-butane/*trans*-2-butene, ±0.007;

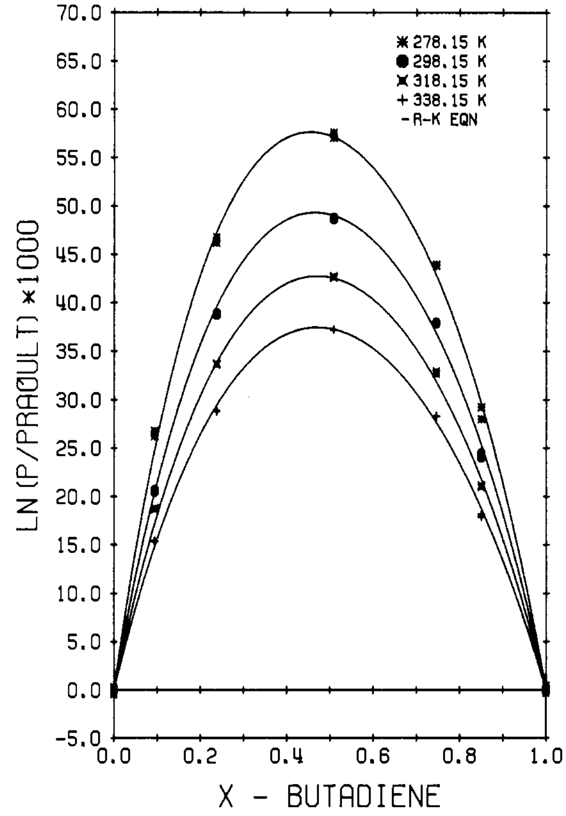

Figure 5. Deviations from Raoult's law for 1,3-butadiene/*n*-butane.

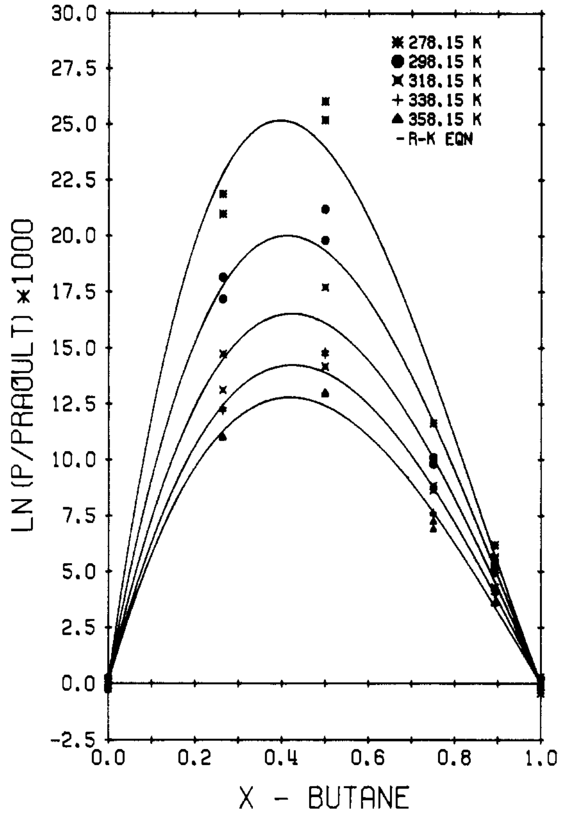

Figure 6. Deviations from Raoult's law for *n*-butane/*cis*-2-butene.

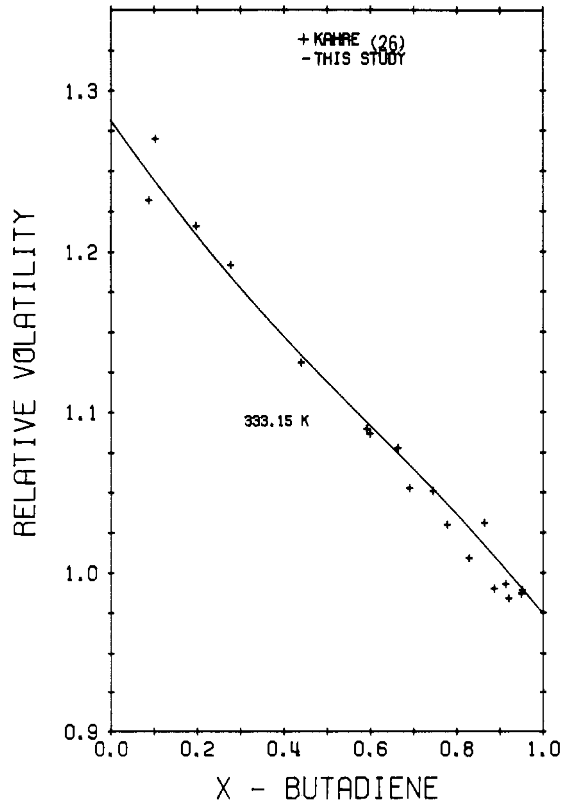

Figure 7. Relative volatilities for 1,3-butadiene/*n*-butane.

n-butane/*cis*-2-butene, ±0.008; *trans*-2-butene/*cis*-2-butene, ±0.005.

A limited amount of literature data on these systems is available. Kahre and Hankinson (*26*) obtained relative volatilities for the three butadiene binaries using the direct sampling technique. These data are presented in Figures 7–9, along with interpolated relative volatilities from this study. Laurance and Swift (*3*) also studied the butadiene/butane binary using the total pressure technique. Figure 10 compares their results with the interpolated results of this study. Agreement with the data of Kahre and Hankinson is generally good, although this study gives slightly lower relative volatilities for low butadiene concentrations in the butadiene/butane binary. The results of Laurance and

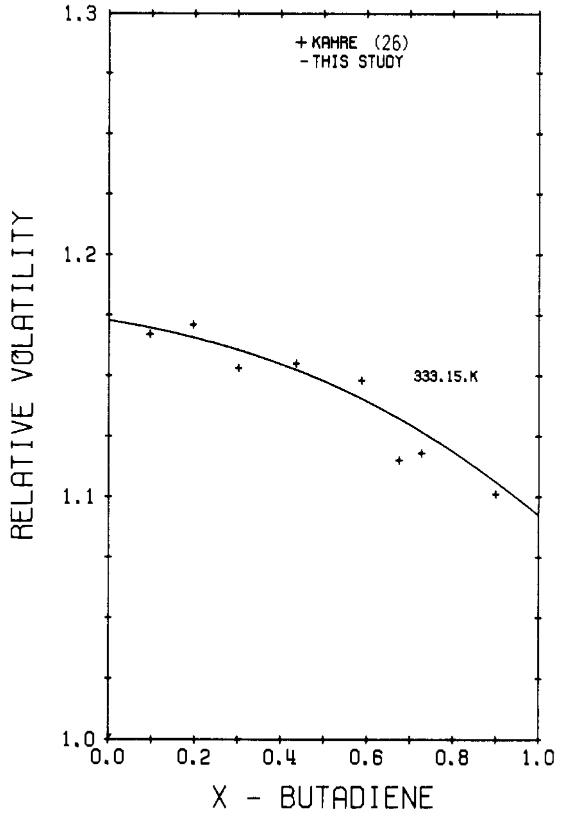

Figure 8. Relative volatilities for 1,3-butadiene/*trans*-2-butene.

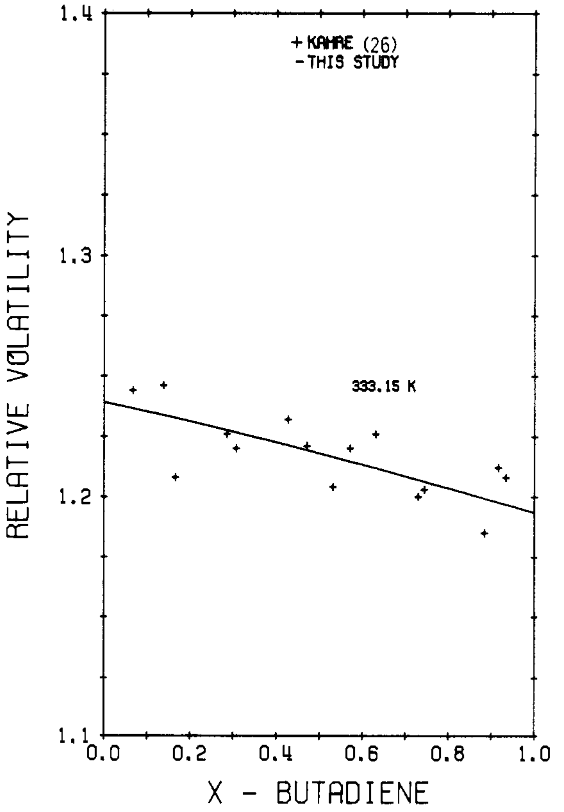

Figure 9. Relative volatilities for 1,3-butadiene/*cis*-2-butene.

Table XI. Redlich-Kister Constants

binary	T, K	B	C	D	P_1, MPa	P_2, MPa
1,3-butadiene (1)/*n*-butane (2)	278.15	0.2292	−0.0319	0.0538	0.144 71	0.124 54
	298.15	0.1967	−0.0220	0.0371	0.281 57	0.243 63
	318.15	0.1706	−0.0169	0.0255	0.499 46	0.434 49
	338.15	0.1494	−0.0153	0.0177	0.824 03	0.720 58
1,3-butadiene (1)/*trans*-2-butene (2)	278.15	0.0550	0.0029		0.144 71	0.118 20
	298.15	0.0502	0.0009		0.281 57	0.233 81
	318.15	0.0440	0.0043		0.499 46	0.421 28
	338.15	0.0370	0.0072		0.824 03	0.704 42
1,3-butadiene (1)/*cis*-2-butene (2)	278.15	0.0252	−0.0117		0.144 71	0.106 59
	298.15	0.0179	−0.0066		0.281 57	0.213 92
	318.15	0.0138	−0.0034		0.499 46	0.389 59
	338.15	0.0120	−0.0014		0.824 03	0.656 79
n-butane (1)/*trans*-2-butene (2)	278.15	0.0717	−0.0250		0.124 54	0.118 20
	298.15	0.0624	−0.0217		0.243 63	0.233 81
	318.15	0.0549	−0.0177		0.434 49	0.421 28
	338.15	0.0489	−0.0134		0.720 58	0.704 42
	358.15	0.0438	−0.0089		1.126 32	1.109 14
n-butane (1)/*cis*-2-butene (2)	278.15	0.0958	−0.0452		0.124 54	0.106 59
	298.15	0.0773	−0.0298		0.243 63	0.213 92
	318.15	0.0644	−0.0213		0.434 49	0.389 59
	338.15	0.0556	−0.0177		0.720 58	0.656 79
	358.15	0.0497	−0.0176		1.126 32	1.039 49
trans-2-butene (1)/*cis*-2-butene (2)	278.15	0.0053			0.118 20	0.106 59
	298.15	0.0039			0.233 81	0.213 92
	318.15	0.0026			0.421 28	0.389 59
	338.15	0.0015			0.704 42	0.656 79
	358.15	0.0006			1.109 14	1.039 49

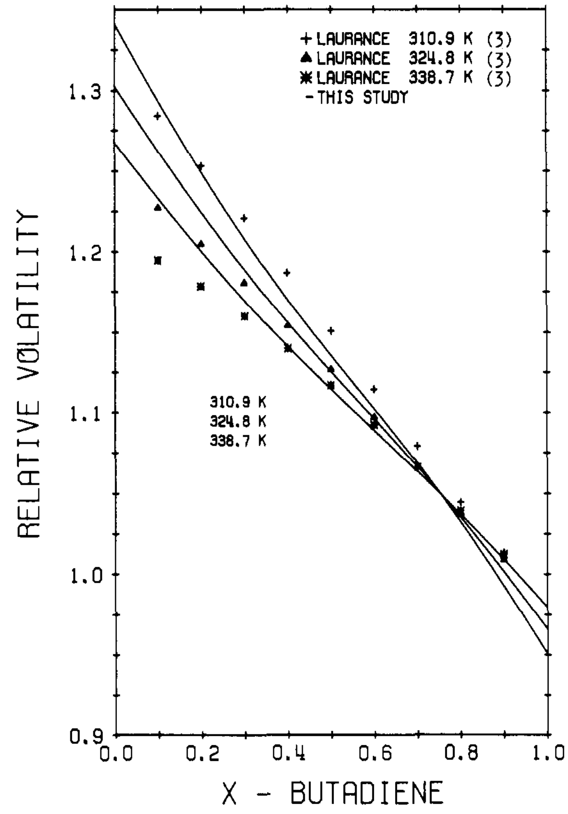

Figure 10. Relative volatilities for 1,3-butadiene/*n*-butane.

Swift are also somewhat higher than those of this study for the same binary.

Conclusions

A significant amount of new vapor pressure data has been determined on systems containing 1,3-butadiene, *n*-butane, *trans*-2-butene, and *cis*-2-butene. Integration of the binary Gibbs–Duhem equation gave relative volatilities with a probable error of no more than ±0.010 unit.

Glossary

A, B, C, D	constants for Goodwin equation
B, C, D	temperature-dependent Redlich–Kister constants
B	second virial coefficient, MPa^{-1}
f	fugacity
P	pressure, MPa
P_R	reference pressure, MPa
R	gas constant, 8.31441×10^{-3} L MPa/(mol K)
T	temperature, K
T_C	critical temperature, K
T_R	reference temperature, K
V	molar volume, L/(g mol)
x_i	mole fraction of component *i* in liquid
x	mole fraction of most volatile component in liquid
y_i	mole fraction of component *i* in vapor
z_i	mole fraction of component *i*
Z	compressibility factor

Greek Letters

α	relative volatility, referenced to more volatile component
ϕ_i	fugacity coefficient of component *i*

Literature Cited

(1) Manley, D. B. Ph.D. Dissertation, University of Kansas, Lawrence, KS, 1970.
(2) Manley, D. B.; Swift, G. W. *J. Chem. Eng. Data* **1971**, *16*, 301.
(3) Laurance, D. R.; Swift, G. W. *J. Chem. Eng. Data* **1974**, *19*, 61.
(4) Steele, K.; Poling, B. E.; Manley, D. B. *J. Chem. Eng. Data* **1976**, *21*, 399.
(5) Martinez-Ortiz, J. A.; Manley, D. B. *J. Chem. Eng. Data* **1978**, *23*, 165.
(6) Walker, S. L. M.S. Thesis, University of Missouri—Rolla, Rolla, MO, 1973.
(7) Steele, K. M.S. Thesis, University of Missouri—Rolla, Rolla, MO, 1975.
(8) Goodwin, R. D. *J. Res. Natl. Bur. Stand. Sect. A* **1974**, *79*, 71.
(9) "Selected Values of Properties of Hydrocarbons and Related Compounds"; American Petroleum Institute, Research Project 44, 1952 and supplements.
(10) Scott, R. B.; Meyers, C. H.; Rands, R. D., Jr.; Brickwedde, F. G.; Bekkedahl, N. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1945**, *35*, 39, RP 1661.

(11) Sage, B. H.; Webster, D. C.; Lacey, W. N. *Ind. Eng. Chem.* **1937**, *29*, 1188.
(12) Dana, L. I.; Jenkins, A. C.; Burdick, J. N.; Timm, R. C. *Refrig. Eng.* **1926**, *12*, 387.
(13) Kay, W. B. *Ind. Eng. Chem.* **1940**, *32*, 358.
(14) Beattie, J. A.; Simard, G. L.; Su, G. J. *J. Am. Chem. Soc.* **1939**, *61*, 24.
(15) Wackher, R. C.; Linn, C. B.; Grosse, A. V. *Ind. Eng. Chem.* **1945**, *37*, 464.
(16) Kistiakowsky, G. B.; Ruhoff, J. R.; Smith, H. A.; Vanghan, W. E. *J. Am. Chem. Soc.* **1935**, *57*, 876.
(17) Lamb, A. B.; Roper, E. E. *J. Am. Chem. Soc.* **1940**, *62*, 806.
(18) Guttman, L.; Pitzer, K. S. *J. Am. Chem. Soc.* **1945**, *67*, 324.
(19) Huisman, J.; Sage, B. H. *J. Chem. Eng. Data* **1964**, *9*, 536.
(20) Scott, R. B.; Ferguson, W. J.; Brickwedde, F. G. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1944**, *33*, 1, RP 1592.
(21) "Technical Data Book", 2nd ed.; American Petroleum Institute, 1970.
(22) Meyers, C. H.; Cargoe, C. S.; Mueller, E. F. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1949**, *39*, 507, RP 1844.
(23) Olds, R. H.; Reamer, H. H.; Sage, B. H.; Lacey, W. N. *Ind. Eng. Chem.* **1944**, *36*, 282.
(24) Sliwinski, P. *Z. Phys. Chem.* **1969**, *63*, 263.
(25) Roper, E. E. *J. Phys. Chem.* **1940**, *44*, 835.
(26) Kahre, L. C.; Hankinson, R. W. *Hydrocarbon Process.* **1972**, *51*, 94.

Received for review September 14, 1981. Accepted May 10, 1982.

Excess Volumes of 1,1,2,2-Tetrachloroethane + Normal Alkanols (C_3–C_8)

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Excess volumes for the binary mixtures of 1,1,2,2-tetrachloroethane with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol have been determined at 303.15 K. The excess function is negative in mixtures rich in alcohols and it becomes positive at different mole fractions of the chloroalkane. The results have been explained in terms of depolymerization of hydrogen-bonded alcohol aggregates, interstitial accommodation of halogenated hydrocarbon in the polymers of alcohols, and weak hydrogen-bond interactions between unlike molecules.

Introduction

We report here new excess volume data for six binary mixtures of 1,1,2,2-tetrachloroethane with 1-alkanols. The alcohols include 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol. The results are examined in the light of depolymerization of alcohols, interstitial accommodation of chloroalkane in hydrogen-bonded alcohol aggregates, possible hydrogen-bond interactions of the type Cl···H–O, between unlike molecules, and the influence of chain length of the alcohol on the aforesaid factors.

Experimental Section

Excess volumes were measured by using the dilatometer described by Rao and Naidu (*1*). 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. All the materials were purified by the methods described by Reddick and Bunger (*2*). 1,1,2,2-Tetrachloroethane (Riedel) was shaken with concentrated sulfuric acid for 10 min at 80–90 °C. The operation was repeated until the acid developed no more color. The chloroalkane was then washed with water, steam distilled, dried with potassium carbonate, and fractionally distilled. 1-Propanol (J. T. Baker) and 1-butanol (BDH) were refluxed over freshly ignited calcium oxide for 6 h and distilled with a fractionating column. 1-Pentanol (J. T. Baker) was dried over Drierite and fractionally distilled. 1-Hexanol (BDH England), 1-heptanol (Koch-Light Laboratories Ltd., England), and 1-octanol (BDH England) were fractionally distilled. A fractionating column that contained 30 theoretical plates was used in all cases. The purity of the samples was checked by comparing the measured densities of the compounds with those reported in the literature (*3*). Densities were determined by using a bicapillary-type pycnometer which offered an accuracy of 2 parts in 10^5.

Results

The experimental excess volumes of the six binary mixtures are given in Table I and are also graphically represented in Figure 1. The dependence of V^E on composition may be expressed by an empirical equation of the form

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

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

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

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0021-9568/82/1727-0412$01.25/0