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Excess Volumes of Tetrachloroethylene with Some Aliphatic and Alicyclic Ketones at 303.15 and 313.15 K

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Excess volumes on mixing for binary mixtures of tetrachloroethylene with aliphatic ketones and alicyclic ketones have been determined dilatometrically. The V^E data are reported over the complete mole fraction range at 303.15 and 313.15 K. Aliphatic ketones include methyl ethyl ketone, methyl propyl ketone, and diethyl ketone, and alicyclic ketones are cyclopentanone and cyclohexanone. An inversion of the sign of V^E is observed over some concentrations for all mixtures except with the methyl ethyl ketone and cyclopentanone at 303.15 K. The V^E values become positive on increasing temperature, except for the mixture methyl propyl ketone with tetrachloroethylene. The observed values are interpreted in terms of dipole-induced dipole interactions between the dipole of the ketone and tetrachloroethylene.

Introduction

The present paper reports measurements of excess volumes for mixtures of tetrachloroethylene with methyl ethyl ketone, methyl propyl ketone, diethyl ketone, cyclopentanone, and cyclohexanone at 303.15 and 313.15 K. These measurements were made as part of a continuing project on the thermodynamic properties of nonelectrolyte solutions (*1-5*).

Experimental Section

Excess volumes were determined directly by the use of a dilatometer described by Rao and Naidu (*6*). The excess volumes are accurate to ±0.003 cm^3 mol^{-1}. The benzene + cyclohexane system at 298.15 K has been suggested as a standard for dilatometry. The measured excess volumes for this system are in good agreement with the earlier values reported in the literature (*7*).

Purification of Materials. Analytical reagent grade tetrachloroethylene was dried over sodium carbonate and fractionally distilled. Methyl ethyl ketone (BDH) and diethyl ketone (BDH) were dried over potassium carbonate for 3 days, then boiled for 2 h, and distilled as reported by Naidu (*8*). Methyl propyl ketone (Fluka) and cyclohexanone (BDH) were purified by the standard method described by Riddick and Bunger (*9*). Cyclopentanone (Fluka) was dried over anhydrous sodium sulfate for 2 days and then fractionally distilled.

Table I. Boiling Points and Densities (ρ) of the Pure Compounds at 303.15 K

	bp, K		ρ, g cm^{-3}	
compd	exptl	lit. (*9*, *10*)	exptl	lit. (*9*, *10*)
tetrachloroethylene	394.28	394.4	1.606 34	1.606 40
methyl ethyl ketone	352.60	352.79	0.794 48	0.794 52
methyl propyl ketone	373.40	373.55	0.796 61	0.796 56
diethyl ketone	375.00	375.15	0.804 60	0.804 61
cyclopentanone	403.70	403.80	0.938 98	0.939 02
cyclohexanone	428.70	428.80	0.937 60	0.937 61

Table II. Excess Volumes of V^E (cm^3 mol^{-1}) of Tetrachloroethylene with Ketones at 303.15 and 313.15 K

303.15 K		313.15 K	
x_A[a]	V^E	x_A[a]	V^E
Tetrachloroethylene + Methyl Ethyl Ketone			
0.1394	−0.017	0.1378	−0.007
0.2039	−0.024	0.2250	0.006
0.3413	−0.037	0.3404	0.035
0.4579	−0.046	0.4718	0.064
0.5401	−0.047	0.5665	0.082
0.5638	−0.046	0.6707	0.089
0.6428	−0.043	0.7559	0.079
0.7318	−0.034	0.8017	0.068
0.8013	−0.026	0.8471	0.055
Tetrachloroethylene + Methyl Propyl Ketone			
0.1515	−0.092	0.1536	−0.104
0.2003	−0.112	0.2376	−0.132
0.2514	−0.122	0.3004	−0.138
0.3417	−0.118	0.3529	−0.128
0.4553	−0.086	0.4239	−0.111
0.5508	−0.055	0.5790	−0.072
0.6429	−0.022	0.6311	−0.058
0.7516	0.011	0.7101	−0.040
0.8031	0.022	0.7666	−0.026
0.8519	0.026	0.8314	−0.010
		0.8801	0.000
		0.9230	0.008
Tetrachloroethylene + Diethyl Ketone			
0.1297	0.034	0.1429	0.022
0.2032	0.000	0.2138	0.030
0.2992	−0.088	0.3604	0.047
0.3770	−0.161	0.4299	0.051
0.4214	−0.198	0.5050	0.046
0.5491	−0.275	0.5813	0.039
0.6216	−0.279	0.6459	0.033
0.7703	−0.214	0.7716	0.021
0.8319	−0.162	0.8329	0.015
Tetrachloroethylene + Cyclopentanone			
0.1409	−0.085	0.1671	−0.035
0.2442	−0.160	0.2505	−0.024
0.3531	−0.237	0.3478	−0.000
0.4686	−0.280	0.4404	0.030
0.5250	−0.285	0.5279	0.050
0.6300	−0.250	0.6478	0.064
0.7229	−0.186	0.7019	0.061
0.7818	−0.139	0.7841	0.053
0.8319	−0.104	0.8514	0.042
Tetrachloroethylene + Cyclohexanone			
0.1505	0.062	0.1492	0.035
0.2368	0.010	0.2182	0.055
0.3599	−0.117	0.3550	0.082
0.4317	−0.194	0.4717	0.099
0.5717	−0.300	0.5523	0.107
0.6503	−0.322	0.6221	0.110
0.7019	−0.315	0.7029	0.107
0.7778	−0.283	0.7887	0.090
0.8305	−0.240	0.8414	0.076
0.8609	−0.208		

[a] Mole fraction of tetrachloroethylene.

The purity of the compounds was checked by measuring densities and boiling points. The densities were measured by using a bicapillary pycnometer which gave an accuracy of 5 parts in 10^5. The boiling points were measured by using a

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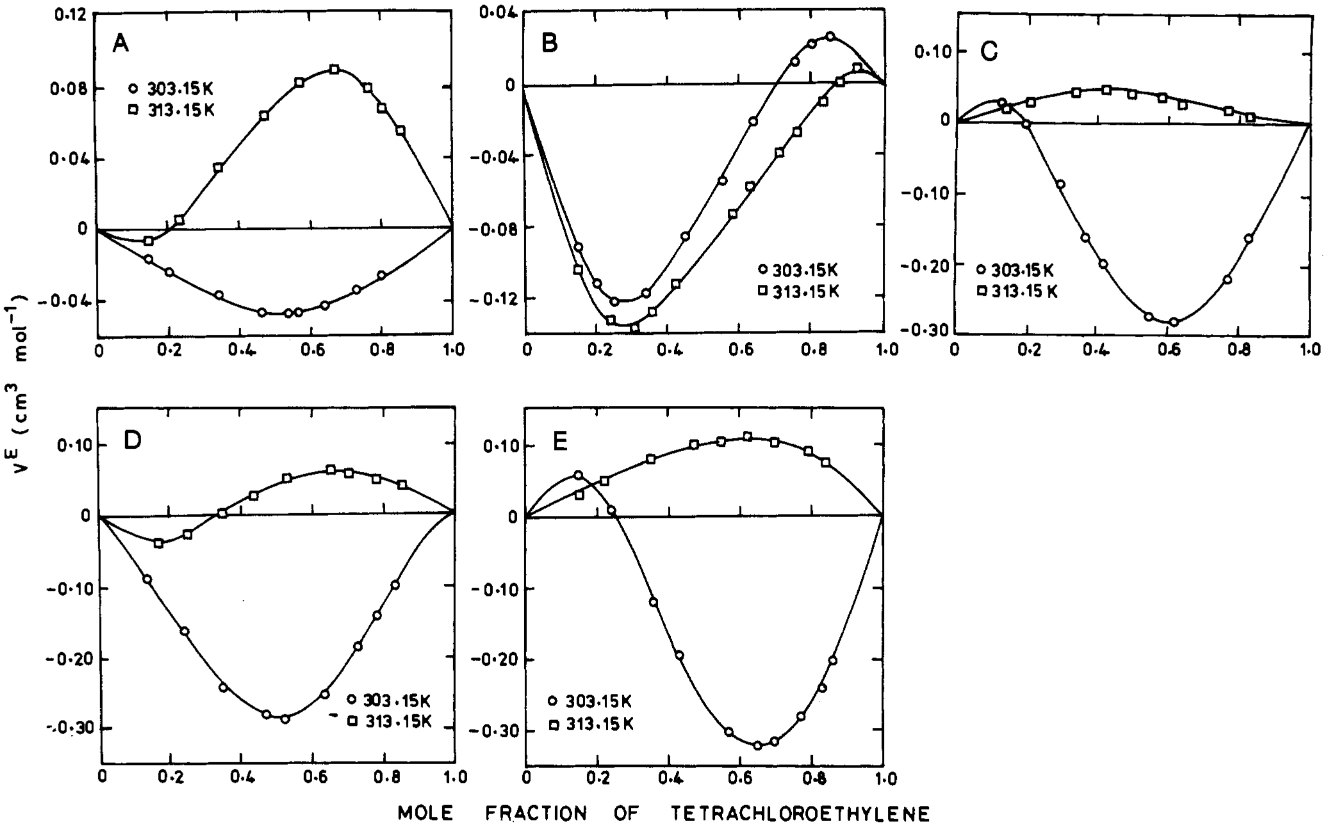

Figure 1. Excess volume-composition curves for tetrachloroethylene with (A) methyl ethyl ketone, (B) methyl propyl ketone, (C) diethyl ketone, (D) cyclopentanone, and (E) cyclohexanone at 303.15 and 313.15 K.

Table III. Values of the Adjustable Parameters a_0, a_1, and a_2 of Eq 1 and the Standard Deviation $\sigma(V^E)$

T, K	a_0[a]	a_1[a]	a_2[a]	σ[a]
Tetrachloroethylene + Methyl Ethyl Ketone				
303.15	−0.1856	−0.0125	0.0782	0.001
313.15	0.2905	0.3492	−0.1987	0.002
Tetrachloroethylene + Methyl Propyl Ketone				
303.15	−0.3019	0.6831	0.0701	0.003
313.15	−0.3893	0.5679	−0.0535	0.005
Tetrachloroethylene + Diethyl Ketone				
303.15	−1.0026	−0.9833	1.1115	0.003
313.15	0.1842	−0.0633	−0.0991	0.003
Tetrachloroethylene + Cyclopentaone				
303.15	−1.1258	0.0121	0.8889	0.004
313.15	0.1716	0.4373	−0.3089	0.002
Tetrachloroethylene + Cyclohexanone				
303.15	−1.0127	−1.5810	0.8122	0.001
313.15	0.4148	0.2059	0.0286	0.001

[a] Units: cm^3 mol^{-1}.

Swietoslawski type ebulliometer which gave an accuracy of ±0.2 K. The measured values are presented in Table I along with the literature values (*9*, *10*).

Results and Discussion

The excess volume-composition data at 303.15 and 313.15 K for tetrachloroethylene mixtures are listed in Table II and these are graphically represented in Figure 1. For each mixture, the excess quantities are fitted by least squares using the polynominal form

$$V^E = x_A(1 - x_A)\sum_{i=0} a_i(2x_A - 1)^i \qquad (1)$$

where x_A refers to the mole fraction of tetrachloroethylene. The adjustable coefficients a_i and corresponding standard deviations σ are given in Table III.

The numerical values of the excess volumes at both temperatures of interest for the tetrachloroethylene with the ketones decrease in the order

methyl ethyl ketone > methyl propyl ketone >
diethyl ketone > cyclopentanone > cyclohexanone

An inversion of the sign of V^E values is observed over part of the concentration range in all the mixtures studied with tetrachloroethylene except for its mixtures with methyl ethyl ketone and cyclopentanone at 303.15 K. The V^E values show a positive temperature coefficient except for the system methyl propyl ketone with tetrachloroethylene. The observed V^E values are due to the existence of specific interactions between the dipole of the ketones and tetrachloroethylene.

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Registry No. Methyl ethyl ketone, 78-93-3; methyl propyl ketone, 107-87-9; diethyl ketone, 96-22-0; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; tetrachloroethylene, 127-18-4.

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Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of Diethylamine with Acetone, Acetonitrile, and Methanol

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Total-pressure vapor–liquid equilibrium (VLE) data are reported at 298, 348, and 398 K for each of the three diethylamine binaries with acetone, acetonitrile, and methanol. The experimental *PTx* data were reduced by both the Mixon–Gumowski–Carpenter and Barker methods; the Mixon et al. results were deemed better and are reported. Six G^E correlations were tested in the Barker data reduction method; the results are reported for the correlation for which the best results were obtained. Various equations of state were used to estimate the vapor-phase fugacity coefficients; the Peng–Robinson results were used for the values reported.

Introduction

Total-pressure vapor–liquid equilibrium data for the three systems covered in this paper were measured as part of the continuing effort to expand the accurate vapor–liquid equilibrium data base for a general correlation of mixture properties. The systems were chosen to cover gaps in the UNIFAC parameter table. Data were measured at three temperatures for all the binaries. The apparatus and technique for the experimental measurements—as well as the defining equation for the activity coefficient and the standard states used—were the same as described by Maher and Smith (*1*).

Chemicals Used

Table I lists the chemicals used and their stated purities. All chemicals were available in at least 99.9% purity. Activated molecular sieves (4 Å) were put into the containers with the chemicals as they were received. The chemicals were vacuum distilled through a Vigreux column (25-mm o.d. and 470 mm long), before they were loaded into the VLE cells. The first and last portions of the distillate were discarded. The retained samples were backflushed with nitrogen and put into amber glass bottles for transfer to the loading operation. The initial

Table I. Chemicals Used

component	vendor	purity, %
diethylamine	Sigma Chemicals	99.9
acetone	Burdick and Jackson	99.9+
acetonitrile	Burdick and Jackson	99.9+
methanol	Fisher Scientific	99.9

Table II. Experimental P vs. x_1 Values for the Diethylamine (1) + Acetone (2) System

298.03 K			347.97 K			398.10 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	30.67	30.67	0.0	184.84	184.81	0.0	677.1	677.1
0.0381	31.70	31.70	0.0380	189.74	189.81	0.0379	693.1	692.7
0.0567	32.14	32.15	0.0567	191.98	191.99	0.0566	697.7	698.3
0.1325	33.69	33.67	0.1324	199.55	199.37	0.1323	719.5	719.1
0.2094	34.78	34.80	0.2093	204.91	205.12	0.2091	736.4	736.7
0.2951	35.65	35.65	0.2950	209.90	209.79	0.2948	751.3	751.2
0.3987	36.27	36.26	0.3987	213.21	213.21	0.3986	761.7	761.7
0.4793	36.50	36.49	0.4792	214.46	214.44	0.4792	765.2	765.0
0.5966	36.45	36.48	0.5966	214.26	214.31	0.5967	762.4	762.7
0.6964	36.14	36.13	0.6965	212.29	212.28	0.6967	753.9	753.6
0.7878	35.47	35.44	0.7879	208.68	208.61	0.7881	739.0	739.1
0.8549	34.59	34.62	0.8550	204.30	204.36	0.8553	724.3	724.2
0.9164	33.54	33.53	0.9165	198.93	198.95	0.9167	705.9	706.0
0.9564	32.63	32.62	0.9565	194.48	194.44	0.9567	691.1	691.0
1.0000	31.37	31.37	1.0000	188.47	188.48	1.0000	672.2	672.2

Table III. Experimental P vs. x_1 Values for the Diethylamine (1) + Acetonitrile (2) System

298.00 K			347.93 K			398.33 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	11.804	11.804	0.0	81.69	81.69	0.0	339.3	339.2
0.0403	15.483	15.485	0.0402	99.95	99.96	0.0400	390.4	390.8
0.0755	18.028	18.023	0.0753	112.96	112.95	0.0750	430.5	430.2
0.1348	21.280	21.286	0.1346	130.28	130.31	0.1342	485.7	485.7
0.2081	24.062	24.057	0.2078	145.96	145.93	0.2074	538.1	538.3
0.2951	26.321	26.329	0.2946	159.43	159.49	0.2939	584.5	584.4
0.3977	28.18	28.17	0.3973	171.09	171.01	0.3968	625.8	625.7
0.4953	29.46	29.47	0.4950	179.15	179.20	0.4945	654.9	654.9
0.5970	30.53	30.53	0.5968	185.61	185.62	0.5964	677.0	677.0
0.6954	31.32	31.32	0.6952	190.25	190.23	0.6950	692.2	692.3
0.7825	31.87	31.87	0.7824	193.18	193.15	0.7824	701.5	701.3
0.8538	32.13	32.14	0.8538	194.25	194.28	0.8539	703.3	703.3
0.9151	32.14	32.14	0.9151	193.78	193.79	0.9152	698.9	699.0
0.9515	31.97	31.97	0.9515	192.40	192.37	0.9516	692.6	692.4
1.0000	31.42	31.42	1.0000	188.59	188.59	1.0000	677.0	677.0

Table IV. Experimental P vs. x_1 Values for the Diethylamine (1) + Methanol (2) System

297.97 K			348.09 K			398.58 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	16.885	16.889	0.0	150.98	151.26	0.0	746.6	746.5
0.0389	16.404	16.392	0.0389	148.35	148.14	0.0389	736.7	736.8
0.0746	15.955	15.955	0.0746	145.98	145.69	0.0747	730.2	730.1
0.1306	15.278	15.304	0.1306	142.72	142.67	0.1306	722.5	722.5
0.1930	14.686	14.669	0.1930	140.32	140.58	0.1930	716.0	716.0
0.2798	14.407	14.383	0.2798	139.85	140.15	0.2798	710.4	710.5
0.3756	15.390	15.432	0.3755	143.67	143.38	0.3756	710.2	710.0
0.4760	17.744	17.731	0.4758	151.02	150.81	0.4759	712.5	712.7
0.5733	20.579	20.561	0.5731	159.37	159.62	0.5733	715.0	714.8
0.6726	23.511	23.528	0.6724	167.89	167.90	0.6727	714.9	715.0
0.7674	26.060	26.061	0.7673	175.26	175.15	0.7675	712.6	712.6
0.8431	27.91	27.91	0.8430	180.55	180.62	0.8433	707.4	707.4
0.9002	29.25	29.24	0.9001	184.28	184.26	0.9004	701.0	700.9
0.9492	30.35	30.36	0.9492	187.21	187.21	0.9494	692.7	692.8
1.0000	31.48	31.48	1.0000	189.88	189.88	1.0000	681.5	681.5

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