

Solute Activity Coefficients at Infinite Dilution and Specific Retention Volumes Measured by Gas-Liquid Chromatography

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Gas-liquid chromatographic specific retention volumes and solute activity coefficients at infinite dilution in the liquid phase have been measured for 273 nonelectrolytic binary systems (39 solutes and seven solvents). All of the solutes are volatile (vapor pressures of all pure substances greater than 100 mm. of Hg), while all of the solvents are nonvolatile (vapor pressures less than 0.1 mm. of Hg) at all operating temperatures.

ACTIVITY COEFFICIENTS determined by gas-liquid chromatography (GLC) are thermodynamically reliable, and they compare quite favorably with those extrapolated from static measurements in bulk liquid under well-defined equilibrium conditions (4, 5). These activity coefficients and their temperature dependence yield much information on the nature of intermolecular forces operative in the liquid phase. In particular, they enable one to gain theoretical insight into the interaction of a solute molecule with the solvent "force field" which completely surrounds it.

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The following expression (8) relates the activity coefficient of the solute at infinite dilution in the liquid phase (γ_2^∞) to the GLC measured specific retention volume (V_g^0):

$$\gamma_2^\infty = \frac{1.704 \times 10^7}{M p_2^0 V_g^0} \quad (1)$$

where

M = molecular weight of the stationary liquid phase (solvent),
 p_2^0 = vapor pressure of the pure saturated solute vapor in mm. of Hg abs.,
 V_g^0 = specific corrected retention volume of the solute in cc. of carrier gas per gram of liquid.

Table I. Specific

At 53.2° C. with Solvent							
	A	B	C	D	E	G	
Benzene	218.8	203.3	190.6	318.0	290.7	205.4	282.8
Toluene	644.5	583.5	540.6	857.8	835.4	538.2	727.1
Cyclopentane	100.7	95.10	69.75	73.24	42.58	40.24	51.08
Methylcyclopentane	190.9	177.0	127.2	134.4	80.10	66.08	87.59
Cyclohexane	265.1	249.4	178.7	187.1	110.1	97.91	121.7
Cyclohexene	293.9	273.6	215.1	244.0	178.3	150.2	180.1
2-Methyl-2-butene	62.51	57.68	43.85	49.33	33.05	23.85	35.68
1-Pentene	44.66	41.02	30.85	35.77	22.05	16.89	25.26
4-Methyl-1-pentene	89.81	81.35	59.81	69.79	42.85	30.25	46.45
2-Methyl-1-pentene	122.7	110.4	83.11	97.02	61.62	43.87	65.15
1-Hexene	126.1	113.6	84.90	98.93	60.34	44.78	66.01
1-Heptene	341.9	302.6	224.3	261.4	158.6	116.0	166.2
Isopentane	40.79	37.51	26.15	27.86	15.83	10.86	17.27
n-Pentane	53.75	48.73	34.38	35.99	20.18	14.82	22.55
2,2-Dimethylbutane	77.45	70.51	48.12	51.59	29.91	18.63	30.78
2,3-Dimethylbutane	105.6	96.15	66.68	70.62	42.28	26.71	42.65
2-Methylpentane	108.7	98.47	68.21	71.61	40.69	27.68	42.75
n-Hexane	149.8	133.0	93.61	97.80	54.50	38.85	57.21
2,2-Dimethylpentane	191.8	171.7	117.2	124.8	69.40	44.57	71.06
2,4-Dimethylpentane	199.5	179.1	121.5	129.1	72.26	46.62	73.76
2,3-Dimethylpentane	301.1	268.9	186.2	197.1	118.3	74.31	113.4
3-Methylhexane	318.3	281.7	194.8	205.4	117.5	77.81	116.7
n-Heptane	406.7	355.9	249.2	259.6	143.6	100.5	144.3
Methyl iodide	55.63	52.61	53.29	92.13	54.21	64.69	75.61
Dichloromethane	43.62	42.46	51.72	172.0	71.03	65.67	119.5
Chloroform	118.1	108.5	145.6	665.9	178.4	141.0	288.1
Carbon tetrachloride	226.6	206.0	179.2	268.8	190.7	151.6	202.5
Dibromomethane	249.8	234.2	293.5	949.4	410.4	465.7	632.8
Bromodichloromethane	284.6	257.9	353.6	1639.6	458.4	411.5	714.6
Bromotrichloromethane	551.3	494.0	473.8	897.4	551.3	499.7	606.3
cis-1,2-Dichloroethylene	95.00	89.47	109.0	350.7	146.6	123.9	242.5
trans-1,2-Dichloroethylene	82.68	76.39	74.60	161.1	77.28	73.65	106.4
Trichloroethylene	314.4	287.4	282.6	613.5	293.8	259.7	380.5
1,2-Dichloroethane	144.0	144.8	159.5	493.2	237.2	250.7	407.1
1,1-Dichloroethane	77.70	74.47	78.24	205.2	99.33	89.75	159.0
1,2-Bromochloroethane	329.3	320.9	354.4	1015.2	507.0	583.0	801.4
1-Chloropropane	62.93	61.08	55.40	94.90	54.92	54.93	82.46
1-Chlorobutane	179.8	170.2	151.6	257.9	149.9	143.7	212.4
2-Chlorobutane	123.5	117.3	102.9	172.7	102.9	91.37	144.0

The assumptions, explicit and implicit, underlying the derivation of Equation 1 have been described by Martire (9, 10). For example, it is assumed that the vapor phase above solution and the pure solute vapor both behave ideally. Furthermore, the pure solute is chosen as the standard state—i.e., $\gamma_2 \rightarrow 1$ as $x_2 \rightarrow 1$, where x_2 is the solute mole fraction.

EXPERIMENTAL

The experimental procedure employed has been described

before (9, 10). Only the salient features will be discussed.

A column packing was prepared consisting of 25% by weight of the stationary liquid phase and 75% by weight of treated 60- to 80-mesh Johns-Manville Chromosorb-P. The columns were made from 3.5 feet of 1/4-inch O.D. stainless steel tubing bent into a U shape and fitted with asbestos sleeves to ensure uniform heating. They were installed in a Perkin-Elmer Model 154B Vapor Fractometer, equipped with a thermistor-type thermal conductivity detector. The column temperature was measured by employing a Pyrotest Potentiometer (Technique Associates, Model 9B) with a calibrated dial, in conjunction with iron-constantan thermo-

Table II. Saturated Vapor Pressures (p_2^0) for the Pure Solute (in Mm.)

	p_2^0 at 53.2° C. p_2^0 at 74.1° C. p_2^0 at 93.9° C.				p_2^0 at 53.2° C. p_2^0 at 74.1° C. p_2^0 at 93.9° C.		
Benzene	306.07	629.60	1141.4	2,3-Dimethylpentane	225.05	467.95	856.18
Toluene	105.40	236.57	460.64	3-Methylhexane	206.60	436.02	807.00
Cyclopentane	863.44	1608.9	2695.0	<i>n</i> -Heptane	160.57	350.45	664.11
Methylcyclopentane	412.46	814.97	1431.2	Methyliodide	1077.4	1977.0	3218.5
Cyclohexane	305.72	619.67	1110.4	Dichloromethane	1200.1	2253.7	3799.5
Cyclohexene	282.25	577.44	1043.1	Chloroform	571.76	1115.2	1938.0
2-Methyl-2-butene	1222.3	2227.7	3664.9	Carbon tetrachloride	352.20	705.18	1253.3
1-Pentene	1592.9	2817.0	4520.7	Dibromomethane	163.16	360.25	692.31
4-Methyl-1-pentene	742.60	1402.3	2374.1	Bromodichloromethane	220.10	464.23	858.58
2-Methyl-1-pentene	594.44	1144.0	1967.7	Bromotrichloromethane	134.74	292.49	554.19
1-Hexene	541.94	1051.6	1819.2	<i>cis</i> -1,2-Dichloroethylene	597.04	1167.0	2021.3
1-Heptene	192.29	410.16	765.82	<i>trans</i> -1,2-Dichloroethylene	910.25	1707.8	2958.0
Isopentane	1686.3	2946.6	4681.3	Trichloroethylene	246.50	515.19	946.83
<i>n</i> -Pentane	1316.1	2366.8	3850.1	1,2-Dichloroethane	263.62	557.47	1037.2
2,2-Dimethylbutane	847.62	1555.1	2570.5	1,1-Dichloroethane	662.66	1286.0	2226.3
2,3-Dimethylbutane	651.83	1229.5	2079.3	1,2-Bromochloroethane	117.00	263.62	514.88
2-Methylpentane	603.57	1155.7	1977.6	1-Chloropropane	944.36	1765.4	2964.3
<i>n</i> -Hexane	454.03	896.68	1573.4	1-Chlorobutane	324.74	663.38	1196.9
2,2-Dimethylpentane	324.25	650.64	1156.4	2-Chlorobutane	458.91	912.04	1609.3
2,4-Dimethylpentane	308.20	624.27	1117.7				

Retention Volumes (V_R^0)

At 74.1° C. with Solvent							At 93.9° C. with Solvent						
A	B	C	D	E	F	G	A	B	C	D	E	F	G
112.7	101.2	103.9	154.8	134.3	116.7	134.8	64.69	56.13	60.87	82.73	68.65	63.22	70.75
296.2	259.8	263.8	379.2	345.4	279.5	315.2	154.0	131.7	140.7	185.0	160.3	140.4	155.6
55.14	50.79	40.20	41.10	23.84	26.67	28.71	33.36	29.77	24.94	24.72	14.30	16.63	17.67
98.22	88.97	69.19	70.95	42.63	41.65	46.58	56.22	49.54	40.76	40.59	24.20	25.03	27.41
133.6	122.8	95.86	96.47	57.88	60.50	64.12	75.32	67.07	55.35	54.34	32.63	35.22	36.78
146.4	133.3	113.0	121.7	87.95	88.40	90.35	81.18	71.95	64.67	66.82	46.88	49.51	50.22
35.08	31.73	25.97	28.43	18.49	16.31	20.36	21.67	18.89	16.51	17.02	10.86	10.21	12.55
26.29	23.34	19.10	20.97	12.90	11.84	15.03	16.65	14.49	12.51	13.26	7.97	7.74	9.46
49.40	43.50	34.75	38.52	23.74	20.16	26.31	29.78	25.64	21.69	23.00	13.93	12.62	15.85
64.63	57.20	46.42	51.17	32.50	27.85	35.11	37.71	32.65	28.04	29.56	18.34	16.81	20.63
66.23	58.41	47.36	52.86	32.02	28.77	35.53	38.59	33.04	28.58	30.15	18.14	17.16	20.84
162.6	141.0	113.3	125.3	76.34	67.41	81.35	86.99	73.44	62.65	66.63	39.99	37.46	44.33
24.25	21.91	16.17	16.51	9.54	7.96	10.68	15.65	13.63	10.76	10.49	6.07	5.42	7.01
30.68	27.49	20.85	21.12	11.93	10.45	13.42	19.19	16.67	13.42	13.06	7.33	6.91	8.59
43.37	38.98	28.59	29.69	17.40	13.22	18.26	26.93	23.26	18.15	18.26	10.66	8.62	11.66
57.34	51.38	38.40	38.86	23.55	18.14	24.31	34.26	29.71	23.67	23.54	13.98	11.51	14.91
58.52	51.78	38.34	39.44	22.45	18.45	24.06	34.52	29.79	23.52	23.04	13.17	11.58	14.71
76.82	68.01	51.15	51.61	29.23	25.21	31.50	44.32	37.85	30.18	29.54	16.70	15.27	18.75
97.85	86.30	63.48	64.97	36.79	28.61	38.56	55.37	47.38	37.17	37.20	21.00	17.37	22.66
100.9	88.79	64.90	66.80	37.90	29.52	39.46	56.86	48.54	37.78	37.50	21.33	17.79	23.00
146.3	129.5	96.61	98.67	59.56	45.77	58.84	80.05	68.69	54.41	53.56	32.39	26.86	33.34
152.4	134.0	99.42	101.0	58.89	47.33	59.73	82.77	70.06	55.43	54.74	31.68	27.45	33.56
188.6	164.0	122.4	124.1	69.84	59.10	72.09	98.96	83.84	66.27	65.51	36.85	33.28	39.39
33.35	30.60	33.18	51.34	30.29	41.47	42.10	21.39	19.07	21.94	30.84	17.95	24.96	25.00
25.58	24.61	31.53	84.41	37.30	40.47	61.24	17.20	15.29	20.49	45.80	20.80	23.45	33.89
64.99	57.92	78.63	276.0	85.85	81.21	133.6	38.73	33.61	46.37	130.0	44.70	44.62	68.61
117.0	104.8	96.41	131.7	94.16	88.27	100.7	66.78	58.09	56.09	71.80	50.11	49.03	54.87
129.9	118.2	155.2	406.2	186.3	244.6	281.7	73.74	64.84	88.94	194.7	92.62	124.0	139.5
144.8	128.5	178.4	630.4	203.0	216.2	306.4	81.23	69.81	98.51	277.7	98.57	109.7	147.5
263.0	233.7	233.9	387.8	247.8	261.2	271.1	141.1	121.3	126.4	189.0	121.6	132.6	135.3
53.17	48.69	61.63	160.2	72.90	72.61	115.8	32.18	28.76	37.38	82.29	38.74	40.12	60.97
46.44	42.23	43.61	79.72	40.59	45.12	54.78	28.34	25.11	27.17	44.29	22.81	26.00	30.82
154.5	139.7	143.9	266.1	138.4	142.9	174.8	85.44	74.70	79.97	130.5	69.82	75.18	88.66
77.82	74.35	89.60	226.5	113.6	137.4	186.8	46.19	41.81	53.82	115.2	58.33	71.70	94.76
44.22	40.89	46.28	100.4	51.45	53.67	79.54	27.61	24.38	28.97	54.70	28.32	30.43	43.31
165.7	154.7	186.0	442.1	230.6	299.3	350.0	92.37	82.18	105.9	215.3	112.8	148.0	170.6
36.27	33.86	33.45	51.80	29.78	34.23	44.16	22.58	20.21	21.52	30.33	17.24	20.08	25.37
92.85	85.15	82.73	127.1	74.25	81.96	103.5	53.37	46.95	48.95	68.31	39.56	44.55	55.07
66.86	61.35	58.88	88.70	53.12	54.41	72.95	39.71	34.79	36.06	49.65	29.34	30.81	40.30

Table III. Solute

	At 53.2° C. with Solvent						
	A	B	C	D	E	F	G
Benzene	0.901	0.648	1.205	0.685	0.460	1.109	0.707
Toluene	0.888	0.655	1.234	0.738	0.465	1.230	0.799
Cyclopentane	0.694	0.491	1.167	1.055	1.114	2.007	1.388
Methylcyclopentane	0.766	0.552	1.340	1.203	1.239	2.559	1.695
Cyclohexane	0.744	0.529	1.287	1.166	1.217	2.330	1.645
Cyclohexene	0.727	0.522	1.158	0.969	0.814	1.645	1.204
2-Methyl-2-butene	0.789	0.572	1.311	1.106	1.014	2.393	1.404
1-Pentene	0.848	0.617	1.430	1.171	1.166	2.592	1.522
4-Methyl-1-pentene	0.904	0.667	1.583	1.287	1.287	3.105	1.775
2-Methyl-1-pentene	0.827	0.614	1.423	1.157	1.118	2.675	1.581
1-Hexene	0.883	0.655	1.528	1.244	1.252	2.874	1.711
1-Heptene	0.917	0.693	1.630	1.327	1.343	3.127	1.916
Isopentane	0.877	0.637	1.594	1.420	1.534	3.808	2.102
<i>n</i> -Pentane	0.853	0.628	1.553	1.408	1.542	3.576	2.063
2,2-Dimethylbutane	0.919	0.674	1.723	1.526	1.615	4.417	2.347
2,3-Dimethylbutane	0.877	0.643	1.617	1.449	1.486	4.006	2.202
2-Methylpentane	0.919	0.678	1.707	1.543	1.667	4.175	2.373
<i>n</i> -Hexane	0.887	0.667	1.654	1.502	1.655	3.954	2.357
2,2-Dimethylpentane	0.970	0.724	1.850	1.649	1.820	4.826	2.657
2,4-Dimethylpentane	0.981	0.730	1.877	1.677	1.839	4.854	2.693
2,3-Dimethylpentane	0.890	0.666	1.677	1.504	1.538	4.171	2.399
3-Methylhexane	0.917	0.693	1.746	1.572	1.687	4.339	2.539
<i>n</i> -Heptane	0.924	0.705	1.757	1.600	1.776	4.322	2.643
Methyliodide	1.006	0.711	1.224	0.672	0.701	1.001	0.752
Dichloromethane	1.152	0.790	1.132	0.323	0.480	0.885	0.427
Chloroform	0.893	0.650	0.844	0.175	0.401	0.865	0.372
Carbon tetrachloride	0.756	0.556	1.114	0.705	0.610	1.306	0.858
Dibromomethane	1.480	1.055	1.468	0.431	0.612	0.918	0.593
Bromodichloromethane	0.963	0.710	0.903	0.185	0.406	0.770	0.389
Bromotrichloromethane	0.812	0.606	1.101	0.552	0.551	1.036	0.749
<i>cis</i> -1,2-Dichloroethylene	1.063	0.755	1.080	0.319	0.468	0.943	0.423
<i>trans</i> -1,2-Dichloroethylene	0.801	0.580	1.035	0.455	0.582	1.040	0.632
Trichloroethylene	0.778	0.569	1.009	0.441	0.565	1.090	0.653
1,2-Dichloroethane	1.589	1.056	1.672	0.513	0.655	1.055	0.570
1,1-Dichloroethane	1.171	0.817	1.356	0.491	0.622	1.173	0.581
1,2-Bromochloroethane	1.565	1.073	1.695	0.562	0.690	1.023	0.653
1-Chloropropane	1.015	0.699	1.343	0.744	0.790	1.345	0.786
1-Chlorobutane	1.033	0.729	1.428	0.797	0.841	1.495	0.888
2-Chlorobutane	1.064	0.749	1.488	0.842	0.867	1.663	0.926

couples attached to various points on the column. Upon reaching thermal equilibrium, the average column temperature remained constant to within $\pm 0.2^\circ\text{C}$. during the course of the day. The carrier gas (helium) flow rate was measured by means of a soap-film meter. The outlet pressure was at all times atmospheric. The inlet pressure was controlled and measured to within ± 1 mm. with a pressure gage calibrated against a mercury manometer. To inject the 0.5- μl . blended samples used in this study, a 1.0- μl . Hamilton syringe was employed.

RESULTS

Data were obtained for 39 solutes, each in seven solvents (in all, 273 binary systems) at three temperatures—53.2°, 74.1°, and 93.9° C. Using the method proposed by Everett and Stoddart (4) and modified by Martire and Pollara (9, 10), the specific retention volumes (V_g^0) were determined from the well-known expression developed by Littlewood and coworkers (7):

$$V_g^0 = \frac{(D)(F)}{(Z)(W)} \frac{273.2}{T_i} \frac{P_o - P_w}{P_o} \frac{3}{2} \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \quad (2)$$

where

V_g^0 = specific retention volume of the solute, cc. of carrier gas per gram of stationary liquid phase.

D = distance on the recorder chart between the air peak and solute peak, inches.

Z = recorder chart speed, inches per min.

F = carrier gas flow rate measured with soap-film meter at column outlet, cc. per min.

W = weight of stationary liquid, grams

T_i = temperature of soap-film meter, ° K.

P_i = column inlet pressure, mm. of Hg abs.

P_o = column outlet pressure, mm. of Hg abs.

P_w = vapor pressure of water at T_i , mm. of Hg abs.

The V_g^0 results are tabulated in Table I. All the solvents used had a minimum purity of 99.0%; they are coded as follows:

Solvent	Source	Molecular Weight
A <i>n</i> -Eicosane	Humphrey-Wilkinson, Inc.	282.54
B Squalane	Eastman Organic Chemicals	422.80
C 1-Hexadecanol	Matheson, Coleman, and Bell	242.44
D <i>N,N</i> -dimethyl myristamide	C. P. Hall and Co.	255.43
E Di- <i>n</i> -butyl tetrachlorophthalate	Esso Research Laboratories	416.15
F Benzyl diphenyl	May and Baker, Ltd.	244.32
G Di- <i>n</i> -butyl phthalate	May and Baker, Ltd.	278.34

To calculate the activity coefficients through Equation 1, the saturated vapor pressures of the pure solutes (p_i^0) were determined at all three temperatures by means of the Antoine equation:

$$\log p_i^0 (\text{in mm. of Hg}) = A - \frac{B}{t + C} \quad (3)$$

where A , B , C are the Antoine constants for the pure solute and t is the temperature in ° C. The constants have been tabulated (1, 2, 6) for most of these compounds over a limited temperature range. In some cases, the constants had to be evaluated by an interpolation procedure on the

Activity Coefficients (γ_2^{∞})

At 74.1° C. with Solvent							At 93.9° C. with Solvent						
A	B	C	D	E	F	G	A	B	C	D	E	F	G
0.850	0.633	1.074	0.685	0.484	0.947	0.721	0.819	0.629	1.012	0.707	0.523	0.967	0.758
0.861	0.656	1.126	0.744	0.501	1.055	0.821	0.850	0.664	1.084	0.783	0.555	1.078	0.854
0.680	0.493	1.087	1.009	1.068	1.625	1.325	0.671	0.502	1.046	1.001	1.063	1.556	1.286
0.753	0.556	1.247	1.154	1.179	2.055	1.613	0.750	0.568	1.205	1.148	1.182	1.947	1.561
0.729	0.529	1.183	1.116	1.142	1.860	1.541	0.721	0.541	1.144	1.106	1.130	1.773	1.499
0.713	0.524	1.077	0.949	0.806	1.366	1.173	0.712	0.537	1.042	0.957	0.837	1.351	1.169
0.772	0.570	1.215	1.053	0.994	1.920	1.350	0.759	0.582	1.162	1.070	1.029	1.864	1.331
0.814	0.613	1.306	1.129	1.127	2.091	1.446	0.801	0.615	1.243	1.113	1.137	1.993	1.432
0.871	0.661	1.442	1.235	1.230	2.467	1.659	0.853	0.662	1.365	1.222	1.238	2.328	1.627
0.816	0.616	1.324	1.140	1.101	2.189	1.524	0.813	0.627	1.274	1.147	1.135	2.109	1.508
0.866	0.656	1.411	1.200	1.216	2.305	1.639	0.859	0.671	1.352	1.216	1.241	2.234	1.615
0.904	0.697	1.513	1.298	1.308	2.523	1.835	0.905	0.717	1.465	1.307	1.337	2.431	1.803
0.844	0.624	1.475	1.371	1.457	2.974	1.945	0.823	0.632	1.395	1.359	1.441	2.749	1.866
0.831	0.619	1.424	1.335	1.450	2.820	1.927	0.816	0.628	1.360	1.327	1.451	2.622	1.851
0.894	0.665	1.581	1.445	1.513	3.393	2.156	0.871	0.674	1.507	1.421	1.494	3.148	2.043
0.856	0.638	1.489	1.396	1.414	3.127	2.048	0.847	0.652	1.428	1.363	1.409	2.194	1.975
0.892	0.674	1.586	1.464	1.578	3.271	2.202	0.883	0.684	1.511	1.464	1.572	3.046	2.105
0.876	0.661	1.532	1.442	1.562	3.085	2.167	0.865	0.677	1.480	1.435	1.558	2.903	2.075
0.947	0.718	1.702	1.578	1.711	3.747	2.440	0.942	0.736	1.635	1.551	1.686	3.472	2.336
0.958	0.727	1.735	1.600	1.731	3.785	2.485	0.949	0.743	1.665	1.592	1.718	3.508	2.381
0.881	0.665	1.555	1.445	1.469	3.256	2.223	0.880	0.685	1.509	1.455	1.477	3.033	2.145
0.908	0.690	1.621	1.515	1.595	3.380	2.351	0.903	0.713	1.571	1.510	1.602	3.148	2.261
0.913	0.701	1.639	1.534	1.673	3.367	2.423	0.918	0.724	1.597	1.533	1.673	3.156	2.340
0.915	0.666	1.072	0.657	0.684	0.851	0.736	0.876	0.657	0.995	0.672	0.709	0.868	0.761
1.007	0.727	0.989	0.351	0.487	0.765	0.444	0.923	0.697	0.903	0.383	0.518	0.783	0.475
0.832	0.624	0.802	0.217	0.428	0.770	0.411	0.804	0.619	0.782	0.265	0.473	0.807	0.460
0.731	0.545	1.034	0.718	0.617	1.121	0.862	0.721	0.554	1.000	0.741	0.652	1.135	0.890
1.289	0.947	1.257	0.456	0.610	0.792	0.603	1.181	0.898	1.142	0.495	0.639	0.812	0.634
0.897	0.676	0.849	0.228	0.435	0.695	0.430	0.865	0.672	0.831	0.280	0.484	0.741	0.483
0.784	0.590	1.027	0.588	0.565	0.913	0.772	0.771	0.600	1.003	0.637	0.607	0.949	0.817
0.972	0.709	0.977	0.357	0.481	0.823	0.453	0.927	0.693	0.930	0.401	0.523	0.860	0.497
0.760	0.559	0.944	0.490	0.591	0.905	0.654	0.716	0.543	0.875	0.509	0.607	0.907	0.672
0.758	0.560	0.948	0.487	0.574	0.947	0.680	0.746	0.570	0.928	0.540	0.619	0.980	0.729
1.390	0.972	1.407	0.528	0.647	0.911	0.588	1.259	0.929	1.259	0.558	0.677	0.938	0.623
1.061	0.766	1.181	0.517	0.619	1.011	0.599	0.981	0.743	1.090	0.548	0.649	1.030	0.635
1.381	0.988	1.433	0.572	0.674	0.884	0.664	1.268	0.953	1.289	0.602	0.705	0.915	0.697
0.942	0.674	1.190	0.730	0.779	1.154	0.785	0.901	0.673	1.102	0.742	0.801	1.172	0.814
0.979	0.714	1.281	0.791	0.831	1.283	0.892	0.944	0.717	1.200	0.816	0.865	1.308	0.929
0.989	0.720	1.325	0.825	0.845	1.406	0.920	0.944	0.720	1.211	0.835	0.867	1.407	0.944

experimental data (6, 11) known as Thomson's method (2). If the experimental data were also lacking, then the constants were determined from the particular Cox Chart for the solute by Dreisbach's method (3). Table II lists the saturated vapor pressures in units of mm. of Hg abs.

Finally, Table III gives the solute activity coefficients at infinite dilution (γ_2^{∞}) as computed from Equation 1. Note the presence of both negative and positive deviations from Raoult's law. These data should provide a useful guide for investigating the nature of intermolecular forces and solute maneuverability in dilute liquid solutions. A physical interpretation, based on solution theory concepts, of some of these results has already been presented (10).

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LITERATURE CITED

- (1) A.P.I. Research Project 44, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related

Compounds," Carnegie Press, Pittsburgh, 1953.

- (2) Dreisbach, R.R., *Advan. Chem. Ser.* **15**, 1955; **22**, 1959; **29**, 1961.
 (3) Dreisbach, R.R., "P-V-T Relationships of Organic Compounds," Handbook Publishers Inc., Sandusky, Ohio, 1953.
 (4) Everett, D.H., Stoddart, C.T.H., *Trans. Faraday Soc.* **57**, 746 (1961).
 (5) Freeguard, G.F., Stock, R., "Gas Chromatography 1962," M. van Swaay, Ed., p. 102, Butterworths, London, 1962.
 (6) Jordan, T.E., "Vapor Pressure of Organic Compounds," Interscience, New York, 1954.
 (7) Littlewood, A.B., Phillips, C.S.G., Price, D.T., *J. Chem. Soc.* **1955**, p. 1480.
 (8) Martire, D.E., *Anal. Chem.* **33**, 1143 (1961).
 (9) Martire, D.E., "Gas Chromatography (Fourth International Symp.)," L. Fowler, Ed., pp. 33-54, Academic Press, New York, 1963.
 (10) Martire, D.E., Pollara, L.Z., "Advances in Chromatography," J.C. Giddings and R.A. Keller, Eds., Marcel Dekker, Inc., New York, 1965 (in press).
 (11) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.

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