

Specific Retention Volumes and Limiting Activity Coefficients of C₄-C₈ Alkane Solutes in C₂₂-C₃₆ n-Alkane Solvents

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The specific retention volumes of 21 hydrocarbon solutes are measured on eight liquid phases at 80°, 100°, and 120°C. The infinite dilution activity coefficients and heats of solution are presented and compared with literature data.

The basic physical process responsible for retention of a solute in gas-liquid partition chromatography is the partition of a solute or solutes between the gas and liquid phases. Because of this fact, much of the thermodynamic information attainable from a normal (static) solubility or vapor-pressure measurement is also obtainable from gas chromatographic retention volume measurements. In particular, numerous authors (1-4, 6, 8, 11, 14-19, 25, 26, 28, 31, 38, 39) have measured infinite dilution activity coefficients and/or other thermodynamic data such as heat of solution, entropy of solution, and partial molar excess enthalpies and entropies.

Hydrocarbon systems have been studied extensively by this method. The activity coefficients of C₄-C₈ hydrocarbon solutes in n-hexadecane, n-heptadecane, and n-octadecane have been measured at lower temperatures (5, 13, 33, 41). The normal hydrocarbons in the range C₂₀-C₃₆ at higher temperatures (>60°C) have been studied by several investigators (20, 32, 42, 45); however, the studies have been limited in scope, and there is little overlap of the data sets. Hicks and Young (20) studied n-butane, n-pentane, and n-hexane on n-tetracosane and n-otacosane; however, each measurement was at a separate temperature so that little correlation of this data is possible because of the temperature dependence of the activity coefficients in low-molecular-weight solvents at low temperatures. For higher molecular-weight systems at higher temperatures, the activity coefficient is generally independent of temperature, because of low values for the partial molar excess enthalpy of these systems. However, at lower temperatures the activity coefficients generally decrease with increasing temperatures; therefore, it is not advisable to compare data sets at different temperatures for low-molecular-weight systems.

Martire and Pollara (32), Young (45), and Tewari et al. (42) all reported activity coefficient data for one or more solvents in the range 80-120°C, and this literature data will be compared with the results of this report in the Discussion section.

Pease and Thorburn (37) have published V_g data for 27 alkane solutes on n-octacosane, n-dotriacontane, and n-hexatriacontane at 80.0°, 100.0°, and 120.0°C. This set of V_g data was used as a reference point for our V_g values, and the comparison will be given in the Discussion section.

In many cases, the activity coefficients and heats of solution have been compared with data obtained from static isotherm, vapor pressure, or solubility data. The general conclusions (12, 40, 43) are that the accuracy of the limiting activity coefficients and heats of solution are

compatible with static data, and that the chromatographic approach offers several advantages over the laborious static methods.

Theoretical

Specific retention volumes. The fundamental datum obtained from retention volume measurements is the specific retention volume (27). This is defined as the volume of carrier gas (at 0°C and mean column pressure) that must pass into a column containing 1 gram of liquid phase and no pressure gradient, in order to elute one-half of an infinitely dilute plug of sample. Equation 1 is the expression for calculating the specific retention volume, V_g, from the retention time, t_r, and the experimental parameters:

$$V_g = (F_c j / w_l) (t_r - t_a) (273.15 / T_m P_o) (P_o - P_w) \quad (1)$$

where F_c (ml/min) is the flow rate of the carrier gas at the outlet pressure, P_o (torr), and room temperature, T_m (K); w_l (grams) is the weight of the stationary phase; t_a (min) is the retention volume of an inert sample, such as air; j is the James and Martin (21) compressibility correction factor; and P_w (torr) is the vapor pressure of pure water at T_m. This equation is applicable only if the flow rate is measured by a soap bubble flow meter and must be modified slightly if other types of flow meters are used.

The partition coefficient has more thermodynamic significance than V_g and is easily calculated from the specific retention volume. Chromatographically, the significant partition coefficient, K, is the ratio of the concentration of solute in the stationary phase, C_l, to the concentration of solute in the mobile phase, C_m. This partition coefficient can be obtained from the V_g data by means of Equation 2:

$$K = T_c V_g \rho_l / 273.15 \quad (2)$$

where T_c (K) represents the column temperature; and ρ_l is the density (g/ml) of the stationary phase at T_c. Although K is the usual partition coefficient used in chromatography, its usefulness is limited because it is not a true thermodynamic equilibrium constant for the partition of the solute between the stationary and mobile phases (22, 35).

The equilibrium constant, k, is defined as the ratio of the mole fraction of solute in the liquid phase to the partial pressure of the solute in the gas phase and is equal to the ratio of the activities of the solute in the two phases in the region where Henry's law is valid.

$$k = M_l V_g / 273.15 R \quad (3)$$

The equilibrium constant, k, can then be used to determine the free energy, enthalpy, and entropy for the partition process.

Infinite dilution activity coefficients. The activity coefficient which describes the deviation from Raoult's law can be readily calculated from Equation 4 (12):

$$\ln \gamma_2^\infty = \ln (273.15 R / V_g P_2^\circ M_l) - P_2^\circ (B_{22} - v_2^\circ) / RT_c \quad (4)$$

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where γ_2^∞ is the infinite dilution activity coefficient of the solute at column temperature; P_2° is the vapor pressure of pure solute at T_c ; B_{22} is the second virial coefficient of the solute; and v_2° is the molar volume of the solute at T_c . For this investigation, we have used the assumption that $|B_{22}| \gg |v_2^\circ|$; therefore, the following approximate equation was used for the calculation of γ_2^∞ :

$$\ln \gamma_2^\infty = \ln (273.15 R / V_g P_2^\circ M_l) - P_2^\circ B_{22} / RT_c \quad (5)$$

The solute vapor pressures were calculated from the Antoine constants tabulated in the most recent API Project 44 publication (44). The virial coefficients, B_{22} , were calculated using the Principle of Corresponding States (7, 34) and the critical constants given in the monograph by Kudchadker et al. (24). The values of the calculated virial coefficients are listed in Table I, along with available measured values from Dymond and Smith (9). The average relative deviation of the calculated and measured value was 1.0% for the straight and branched chain hydrocarbons.

Enthalpy of solution. If the true thermodynamic equilibrium constant for the solution process, k , is used, the free energy, enthalpy, and entropy of solution can be calculated from Equations 6–8 (35):

$$\Delta G^\circ = -RT \ln k \quad (6)$$

$$\Delta H^\circ = -R \frac{d \ln V_g}{d(1/T)} \quad (7)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T \quad (8)$$

The quantities ΔG° , ΔH° , and ΔS° refer to the transformation

Hypothetical ideal gas (Pressure = 1 atm) \rightarrow Hypothetical pure liquid solute (Fugacity = Henry's law constant)

and the standard state for the liquid phase is the hypothetical pure liquid solute with the infinitely dilute solution as the reference state (35). This is not the same standard state used for the activity coefficient calculations.

The activity coefficients are calculated based on Raoult's law as a reference for the solute in solution, and the standard state is the real pure liquid solution. This duality of standard states has been previously pointed out by several investigators (22, 35, 36).

Excess thermodynamic functions. The partial molar excess free energies can be calculated from the Raoult's law activity coefficient, γ_2^∞ by means of Equations 9–11:

$$G^e = RT \ln \gamma_2^\infty \quad (9)$$

$$H^e = R \frac{d \ln \gamma_2^\infty}{d(1/T)} \quad (10)$$

$$S^e = (H^e - G^e) / T \quad (11)$$

We have not tabulated all of these values in this paper; however, all of the various thermodynamic functions can be calculated from the salient data presented in the Results section.

Retention indices. The Kovats retention index (10, 23) of a solute is an alternative to the specific retention volume and is a commonly used method for expressing retention volume data. The retention index, I , of a solute is defined as

$$I = 100 \left\{ \frac{\log V_{gx} - \log V_{gn}}{\log V_{g(n+1)} - \log V_{gn}} \right\} + 100n \quad (12)$$

where V_{gx} , V_{gn} , and $V_{g(n+1)}$ are the specific retention volume of the solute, the next lower n -alkane, and the next higher alkane, respectively, i.e., $V_{gn} \leq V_{gx} \leq V_{g(n+1)}$; and n represents the carbon number of the n -alkane solutes. The increments $(\log V_{g(n+1)} - \log V_{gn})$ are independent of n and can be evaluated from the slope, b , of a plot of $\log V_{gn}$ vs. n . Thus, Equation 12 can be written as

$$I = (100/b)(\log V_{gx} - \log V_{gn}) + 100n \quad (13)$$

Experimental

Instrumentation. The chromatograph used for this study was a Beckman GC-65 with a thermal conductivity

Table I. Comparison of Calculated Virial Coefficients with Literature Values (9)
Virial coefficients, $-B_{22}$ (l./mol)

Solute	Abbrev	80°C		100°C		120°C	
		This work	Lit (9)	This work	Lit (9)	This work	Lit (9)
<i>n</i> -Butane	<i>n</i> -C4	0.485	0.485	0.429	0.431	0.382	0.384
<i>n</i> -Pentane	<i>n</i> -C5	0.766	0.778	0.672	0.679	0.594	0.600
<i>n</i> -Hexane	<i>n</i> -C6	1.196	1.188	1.037	1.031	0.910	0.890
<i>n</i> -Heptane	<i>n</i> -C7	1.759	1.766	1.510	1.496	1.312	1.284
<i>n</i> -Octane	<i>n</i> -C8	2.480		2.108	2.122	1.815	1.778
<i>n</i> -Decane	<i>n</i> -C10	3.414		2.852		2.417	
2-Methylbutane	2-MB	0.733	0.738	0.644	0.642	0.570	0.577
2-Methylpentane	2-MP	1.126		0.978		0.859	
2-Methylhexane	2-MHx	1.632		1.403		1.221	
2-Methylheptane	2-MHp	1.928		1.650		1.430	
3-Methylpentane	3-MP	1.167		1.013		0.889	
3-Methylhexane	3-MHx	1.603		1.377		1.197	
3-Methylheptane	3-MHp	2.276		1.936		1.669	
4-Methylheptane	4-MHp	2.309		1.965		1.964	
2,2-Dimethylbutane	2,2-DMB	1.054		0.916		0.805	
2,3-Dimethylbutane	2,3-DMB	1.112		0.966		0.848	
2,2,3-Trimethylbutane	2,2,3-TMB	2.135		1.816		1.565	
2,2-Dimethylpentane	2,2-DMP	1.526		1.314		1.145	
2,3-Dimethylpentane	2,3-DMP	1.576		1.354		1.177	
3,3-Dimethylpentane	3,3-DMP	1.653		1.420		1.234	
2,2,4-Trimethylpentane	2,2,4-TMP	2.066		1.763		1.524	

Table II. List of Solvents (Liquid Phases) and Their Abbreviations

Name	Abbrev
<i>n</i> -Cosane	<i>n</i> -C20
<i>n</i> -Docosane	<i>n</i> -C22
<i>n</i> -Tetracosane	<i>n</i> -C24
<i>n</i> -Octacosane	<i>n</i> -C28
<i>n</i> -Triacontane	<i>n</i> -C30
<i>n</i> -Dotriacontane	<i>n</i> -C32
<i>n</i> -Tetracontane	<i>n</i> -C34
<i>n</i> -Hexatriacontane	<i>n</i> -C36

Table III. Variation of Specific Retention Volume of *n*-Hexane in *n*-Dotriacontane (*n*-C32) at 80°C as Function of Sample Size

Sample size, μ l	V_g , ml/g
2.00	56.19
1.00	56.62
0.50	56.86
0.25	56.86
0.10	56.90
Reported value 56.88	

Table IV. Variation of Specific Retention Volume of *n*-Butane in *n*-Dotriacontane (*n*-C32) at 80°C as Function of Flow Rate

Flow rate, ml/min	V_g , ml/g
34.32	9.65
29.85	9.58
24.69	9.56
20.19	9.57
13.96	9.51
Average 9.57	
Relative mean deviation 0.34%	

Table V. Specific Retention Volumes at 80°C

Solutes	Solvents							
	C-20	C-22	C-24	C-28	C-30	C-32	C-34	C-36
<i>n</i> -C4	11.48	10.69	10.34	9.95	9.29	9.57	9.22	9.05
<i>n</i> -C5	27.78	26.81	26.55	25.36	24.04	24.01	22.69	22.34
<i>n</i> -C6	68.63	64.06	63.14	60.32	57.41	56.88	53.79	52.65
<i>n</i> -C7	162.3	150.9	148.5	141.6	134.7	132.6	125.7	122.8
<i>n</i> -C8	380.9	349.5	347.3	330.7	313.2	308.2	291.0	284.2
<i>n</i> -C10	2050.	1875.	1883.	1747.	1658.	1594.	1542.	1529.
2-MB	22.95	21.23	21.19	20.21	19.08	19.09	17.94	17.57
2-MP	53.10	49.20	49.09	46.41	44.33	43.63	41.26	40.25
2-MHx	122.5	113.4	111.6	106.5	100.8	99.37	94.09	91.64
2-MHp	284.3	259.9	257.7	244.1	231.4	227.1	215.6	210.4
3-MP	60.26	55.81	55.79	52.53	50.28	49.91	47.13	46.00
3-MHx	131.6	123.3	123.0	115.7	110.3	109.0	102.8	100.0
3-MHp	300.3	277.3	277.0	258.6	247.8	243.1	230.7	224.5
4-MHp	288.3	267.4	265.6	251.1	237.2	232.9	220.6	214.5
2,2-DMB	40.37	37.41	37.32	34.77	33.26	33.04	31.28	30.52
2,3-DMB	51.95	48.49	48.52	45.77	43.67	43.27	41.23	40.40
2,2,3-TMB	99.00	91.29	91.79	86.65	82.43	81.71	77.33	75.27
2,2-DMP	87.20	80.48	80.21	75.23	71.44	70.52	67.10	65.30
2,3-DMP	127.7	119.6	118.9	112.5	107.3	105.9	100.8	97.96
3,3-DMP	116.4	108.1	108.1	101.4	97.20	96.48	91.12	88.94
2,2,4-TMP	152.1	140.9	140.7	131.0	124.9	122.6	116.4	113.0
Solvent density	0.7481	0.7542	0.7608	0.7672	0.7697	0.7723	0.7742	0.7773
10b values	3.74	3.73	3.75	3.73	3.73	3.68	3.70	3.70
Equation 13								

detector. The column oven temperature was monitored by a precision thermometer inserted into the center of the oven compartment. The column temperature was constant ($\pm 0.1^\circ\text{C}$) for extended periods.

The analog output from the chromatograph was registered on a recorder and concurrently digitized by a Beckman 3111 Autopro intercoupler. The digitized output was transmitted directly to a PDP/10 computer which echoed the output to a teletype set in the laboratory. Alternately, the output of the intercoupler could be stored on punched paper tape, and the tape read into the computer at a later time.

Chromatographic systems. The solutes and their abbreviations are given in Table I and the solvents or liquid phases are given in Table II. The purity of the solutes was not important; however, each solvent was chromatographed on SE-30; and if it was found to be impure, the solvent was recrystallized from chloroform until only one peak was obtained on an SE-30 column.

The solid support used for all of the columns was 60/80 mesh acid washed Chromosorb P from Applied Science Laboratories, Inc., and the columns were made of 2-m \times 0.25-in. o.d. copper tubing.

The liquid loading on each solid support was determined by an ashing technique suggested by Martire (33). The relative deviation of triplicate analyses was always in the range 0.2–0.5%. Several of the columns containing the lower molecular-weight liquid phases were destroyed, the coated support was weighed at the termination of the experiments, and in no case was a measurable loss of liquid phase detected.

Precautions required for meaningful thermodynamic measurements by gas chromatography. There are several factors which can cause the specific retention volume to differ from the thermodynamic relationships given in Equations 2 and 3, and these factors must be eliminated in order for the V_g data to have significance. Nonlinear isotherms, nonequilibrium effects, and liquid and/or solid surface adsorption of the solute are the primary maleficent effects which must be avoided.

The partition isotherms for hydrocarbon systems are linear at very low solute concentrations. That is, K and k will be constant for small sample sizes; this can be proved by showing that V_g is independent of sample size used in the study.

Nonequilibrium effects which merely increase the width of the peak have no effect on V_g values and can be minimized by using a flow rate which corresponds to

the "optimum velocity." Effects which influence V_g can be detected by the variation of V_g with flow rate.

Liquid and solid surface adsorption have not been observed for hydrocarbon solutes and hydrocarbon solvents. However, adsorption phenomena are easily detected from the peak shape and the variation of V_g with liquid phase loading and/or solute sample size.

Procedure. The solutes were injected in mixtures of

Table VI. Specific Retention Volumes at 100°C

Solutes	Solvents						
	C-22	C-24	C-28	C-30	C-32	C-34	C-36
<i>n</i> -C4	7.42	7.82	6.84		6.31	6.18	6.19
<i>n</i> -C5	16.97	17.50	15.58	14.89	14.38	14.24	14.11
<i>n</i> -C6	36.67	36.54	33.50	32.71	31.44	31.03	30.78
<i>n</i> -C7	78.75	79.30	72.09	70.21	67.17	66.34	65.95
<i>n</i> -C8	168.5	175.1	154.8	150.2	142.8	141.0	140.1
<i>n</i> -C9	391.6	367.9	337.4	321.9	300.0	296.2	295.4
<i>n</i> -C10	823.9	776.8	707.0	677.5	630.0	620.3	618.5
2-MB	13.70	13.96	13.22	12.27	11.71	11.71	11.47
2-MP	29.02	29.10	26.60	25.90	24.83	24.59	24.23
2-MHx	61.45	61.58	55.87	54.41	52.07	51.32	50.89
2-MHp	129.6	135.0	118.4	115.1	109.7	107.9	107.2
3-MP	32.77	34.52	30.24	29.38	28.23	27.90	27.53
3-MHx	66.53	66.22	60.72	59.16	56.52	56.04	55.49
3-MHp	138.0	143.0	125.7	122.8	116.7	114.8	114.3
4-MHp	132.8	137.9	121.0	117.1	111.7	110.3	109.4
2,2-DMB	22.81	22.94	21.01	20.57	19.63	19.24	19.09
2,3-DMB	29.06	29.01	26.73	26.06	25.04	24.61	24.41
2,2,3-TMB	52.12	54.57	47.82	46.71	44.62	44.02	43.69
2,2-DMP	45.75	45.82	41.62	40.40	38.82	38.03	37.70
2,3-DMP	65.18	65.16	60.06	58.36	55.90	55.22	54.76
3,3-DMP	60.18	63.13	55.21	53.97	51.68	50.97	50.58
2,2,4-TMP	76.25	75.87	68.87	67.15	64.21	63.01	62.40
Solvent density	0.7407	0.7481	0.7541	0.7564	0.7589	0.7607	0.7641
10b values	3.40	3.33	3.35	3.31	3.32	3.32	3.32
Equation 13							

Table VII. Specific Retention Volumes at 120°C

Solutes	Solvents						
	C-22	C-24	C-28	C-30	C-32	C-34	C-36
<i>n</i> -C4	5.63		5.00	4.81	4.78	4.69	4.55
<i>n</i> -C5	11.84	11.39	10.61	10.33	9.91	9.86	9.62
<i>n</i> -C6	24.22	23.43	21.78	21.11	20.12	20.00	19.54
<i>n</i> -C7	48.92	47.24	43.58	42.23	40.44	40.16	38.67
<i>n</i> -C8	97.68	93.42	86.54	84.05	79.96	79.12	76.83
<i>n</i> -C9		185.0	171.0	161.0	156.8	155.5	151.2
<i>n</i> -C10		377.5	335.9	316.6	306.4	306.3	295.5
2-MB	9.96	9.67	8.93	8.68	8.38	8.22	8.01
2-MP	19.78	19.17	17.65	17.03	16.38	16.27	15.83
2-MHx	39.01	37.65	34.68	33.57	32.13	31.85	30.82
2-MHP	77.40	74.09	68.17	66.23	63.24	62.42	60.60
3-MP	21.99	21.25	19.59	19.18	18.24	18.28	17.75
3-MHx	41.94	40.86	37.41	36.36	34.62	34.38	33.45
3-MHp	81.18	78.16	71.53	70.47	66.32	66.20	63.96
4-MHp	78.65	75.89	69.29	67.61	64.32	63.56	62.04
2,2-DMB	15.97	15.44	14.23	13.87	13.23	13.17	12.75
2,3-DMB	19.75	19.27	17.76	17.33	16.49	16.41	16.09
2,2,3-TMB	34.03	32.97	30.32	29.61	28.21	28.15	27.40
2,2-DMP	29.88	29.01	26.47	25.88	24.57	24.51	23.78
2,3-DMP	41.31	40.32	37.06	36.08	34.30	34.36	33.60
3,3-DMP	38.71	37.54	34.42	33.75	32.09	32.07	31.20
2,2,4-TMP	47.84	46.45	42.25	41.14	38.97	38.86	37.75
Solvent density	0.7273	0.7354	0.7411	0.7430	0.7454	0.7470	0.7508
10b value	3.09	3.03	3.03	3.01	3.01	3.01	3.01
Equation 13							

3–6 components at a total sample size of 0.1–0.5 μl , so that the effective sample size was in the range 0.02–0.20 μl . The effect of sample size on the specific retention volume is shown in Table III for *n*-hexane on *n*-dotriacontane at 80°C. The V_g values are constant ($\pm 0.05\%$) for sample sizes of less than 0.5 μl for an individual solute. Thus, the sample sizes used in this study are well below the limit for the range of "infinite dilution."

Each solute was used as a component of two different mixtures, and each mixture was injected twice, so that four values of V_g were averaged for each data point, and V_g for the solutes was independent of the other components in the mixture.

Nonequilibrium effects normally cause skewed peaks and a decrease in V_g at high flow rates. The chromatographic peaks for all of the solutes were symmetrical, and the data in Table IV show that V_g was independent of flow rate in the range $13 \leq F_c \leq 35$ ml/min. Thus, the data measured are true equilibrium values.

Hydrocarbon solutes do not absorb on the surface of Chromosorb P, as shown by the symmetrical elution peaks and the variation of V_g with sample size. Adsorption of the solute at the liquid-gas interface can be detected by a variation of V_g with liquid surface area, i.e., liquid-phase loading (29, 30). The liquid-phase loadings in this study varied from 12 to 18%, and no systematic variation of V_g was observed for different liquid loadings of the same liquid phase.

Results

The values for the specific retention volumes of 22 solutes on 7–8 liquid phases at 80.0°, 100.0°, and 120.0°C are presented in Tables V, VI, and VII, respectively. The infinite dilution activity coefficients did not vary systematically with temperature even for the lightest solutes in *n*-cosane at 80°C. The average values of γ_2^∞ for the three temperatures are given in Table VIII. Plots of $\ln V_g$ vs. $1/T$ were all linear, and the results of the regression analyses for ΔH° for each solute in each liquid phase are given in Table IX.

Discussion

At 80.0°C, the V_g data are in excellent agreement with the values published by Pease and Thorburn (37) and Tewari et al. (42) as shown in Table X. However, at 100° and 120°C, there was a systematic deviation of this data from that of Pease and Thorburn with the V_g values being consistently less than the literature values (37). However, Tewari et al. published V_g values at 76.0°, 80.0°, 84.0°, and 88.0°C, and a linear extrapolation of this data is in excellent agreement with our data at 100° and

Table IX. Enthalpies of Solution ($-\Delta H^\circ$) for Range 80–120°C (kcal/mol)

Solutes	Solvents						
	C-22	C-24	C-28	C-30	C-32	C-34	C-36
<i>n</i> -C4	4.43	4.66	4.75	4.54	4.57	4.67	4.75
<i>n</i> -C5	5.64	5.83	6.02	5.83	5.78	5.76	5.82
<i>n</i> -C6	6.72	6.84	7.04	6.91	6.84	6.83	6.84
<i>n</i> -C7	7.78	7.91	8.14	8.01	7.86	7.88	7.97
<i>n</i> -C8	8.81	9.06	9.26	9.08	8.98	8.99	9.03
<i>n</i> -C9		10.0	9.91	10.1	9.46	9.39	9.76
<i>n</i> -C10	10.8	11.1	11.4	11.4	11.0	11.2	11.3
2-MB	5.23	5.41	5.63	5.44	5.35	5.39	5.42
2-MP	6.30	6.49	6.68	6.61	6.43	6.43	6.44
2-MHx	7.37	7.50	7.75	7.59	7.46	7.48	7.52
2-MHp	8.37	8.60	8.81	8.64	8.49	8.56	8.59
3-MP	6.43	6.65	6.81	6.65	6.61	6.54	6.57
3-MHx	7.45	7.61	7.80	7.66	7.58	7.56	7.56
3-MHp	8.49	8.73	8.88	8.68	8.63	8.62	8.66
4-MHp	8.45	8.64	8.89	8.67	8.55	8.59	8.56
2,2-DMB	5.88	6.09	6.17	6.04	5.98	5.97	6.02
2,3-DMB	6.20	6.38	6.54	6.38	6.32	6.36	6.35
2,2,3-TMB	6.86	7.06	7.25	7.07	7.00	6.98	6.97
2,2-DMP	6.84	7.02	7.22	7.01	6.94	6.96	6.97
2,3-DMP	7.34	7.47	7.67	7.53	7.45	7.43	7.39
3,3-DMP	7.09	7.29	7.46	7.30	7.26	7.21	7.23
2,2,4-TMP	7.46	7.65	7.82	7.67	7.58	7.58	7.57

Table VIII. Averaged Values of Infinite Dilution Activity Coefficients

Solutes	Solvents							
	C-20 ^a	C-22	C-24	C-28	C-30	C-32	C-34	C-36
<i>n</i> -C4	0.830	0.805	0.739	0.693	0.681	0.639	0.619	0.594
<i>n</i> -C5	0.835	0.816	0.753	0.698	0.680	0.654	0.631	0.606
<i>n</i> -C6	0.872	0.859	0.801	0.736	0.712	0.689	0.665	0.639
<i>n</i> -C7	0.899	0.893	0.831	0.768	0.743	0.721	0.696	0.672
<i>n</i> -C8	0.922	0.927	0.854	0.796	0.772	0.753	0.728	0.701
<i>n</i> -C10	0.969	0.950	0.895	0.845	0.830	0.817	0.782	0.751
2-MB	0.861	0.846	0.779	0.710	0.699	0.674	0.652	0.629
2-MP	0.891	0.881	0.816	0.755	0.731	0.708	0.683	0.660
2-MHx	0.919	0.912	0.850	0.787	0.763	0.740	0.715	0.691
2-MHp	0.937	0.940	0.865	0.812	0.786	0.765	0.740	0.714
3-MP	0.856	0.847	0.772	0.726	0.699	0.678	0.652	0.630
3-MHx	0.901	0.884	0.820	0.761	0.735	0.715	0.689	0.666
3-MHp	0.927	0.924	0.849	0.801	0.768	0.753	0.725	0.700
4-MHp	0.930	0.925	0.850	0.800	0.776	0.756	0.731	0.704
2,2-DMB	0.896	0.888	0.823	0.765	0.736	0.714	0.690	0.666
2,3-DMB	0.862	0.847	0.783	0.723	0.698	0.676	0.652	0.625
2,2,3-TMB	0.884	0.882	0.805	0.757	0.730	0.708	0.683	0.658
2,2-DMP	0.938	0.930	0.862	0.804	0.777	0.755	0.728	0.703
2,3-DMP	0.870	0.856	0.793	0.733	0.708	0.688	0.661	0.636
3,3-DMP	0.856	0.849	0.774	0.731	0.701	0.681	0.656	0.632
2,2,4-TMP	0.969	0.959	0.890	0.834	0.805	0.785	0.757	0.732

^a Data at 80°C only.

Table X. Comparison of Specific Retention Volumes with Literature Data at 80°C

Solvent	Relative mean deviation, %		
	Pease and Thorburn (37)	Tewari et al. (42)	Meyer et al. (36)
<i>n</i> -C24	...	1.28	1.22 ^a
<i>n</i> -C28	0.84
<i>n</i> -C30	...	0.83	...
<i>n</i> -C32	1.27
<i>n</i> -C36	0.83	0.84	...

^a Four solutes only (*n*-C5 to *n*-C8).

Table XI. Comparison of ΔH° Values for *n*-C24 Calculated from Equation 17 with Literature Values

Solute	$-\Delta H^\circ$, cal/mol		
	Meyer (35)	This work	Rel dev, %
<i>n</i> -C6	6.77	6.84	1.0
2-MP	6.46	6.49	0.5
2,2-DMB	5.73	6.09	5.9
<i>n</i> -C7	8.08	7.91	2.1
<i>n</i> -C8	9.08	9.06	0.2
<i>n</i> -C9	10.07	10.00	0.7
Average 1.7			

Table XII. Relative Mean Deviations (%) of Infinite Dilution Activity Coefficient Data from Data of Tewari et al. (42) and Young (45)

Solute	<i>n</i> -C24	<i>n</i> -C24	<i>n</i> -C30	<i>n</i> -C36
	(28)	(31)	(31)	(31)
<i>n</i> -C4	8.0
<i>n</i> -C5	1.3
<i>n</i> -C6	2.6	1.0	1.8	0.9
2-MP	...	0.2	1.1	1.1
2,2-DMB	...	0.5	0.4	0.9
2,3-DMB	...	0.8	1.0	0.3
3-MP	...	1.0	1.0	0.2
<i>n</i> -C7	2.0	1.9	3.2	3.3
3-MHx	...	0.4	2.0	1.5
<i>n</i> -C8	2.4	0.5	4.7	3.1
3-MHp	...	0.8	3.4	2.1
Average	3.3	0.8	2.3	1.5

120°C. Figure 1 shows one example of this agreement for *n*-octane in *n*-hexatriacontane. The solid, heavy line in this figure is the regression line for Martire's data at the four lower temperatures. This agreement is also illustrated by a comparison of ΔH° values calculated from Equation 7. Table XI gives the values of ΔH° calculated by Meyer (35) from the Tewari et al. (42) data compared with the ΔH° values calculated from this work, and the agreement is within 1.7% relative deviation.

Young (45) and Tewari et al. (42) have both published activity coefficient data for *n*-alkane solutes in *n*-tetracosane at 80°C. Figure 2 is a plot of $-\log \gamma_2^\infty$ vs. solute carbon number to show the excellent agreement of our data with both sets of previous data. Table XII gives the relative deviation of this data from the data of Tewari et al. (42) and Young (45), and the agreement is in the range of 0.2–8.0% with an average of about 1.5%.

The activity coefficients measured in this investigation were independent of temperature. This has been ob-

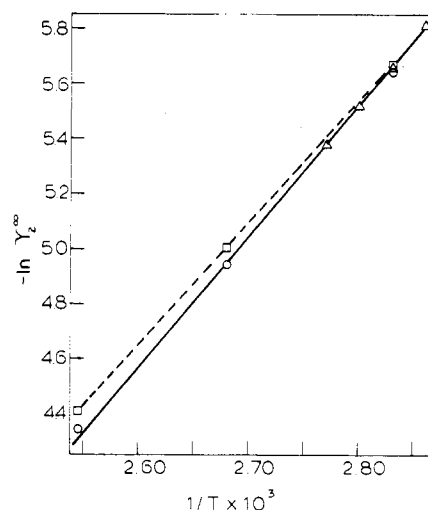


Figure 1. Plot of $-\ln \gamma_2^\infty$ vs. $1/T$ for *n*-octane in *n*-hexatriacontane

○ This work
 □ Pease and Thorburn (37)
 △ Tewari et al. (42)
 — Regression line for data from ref. 42

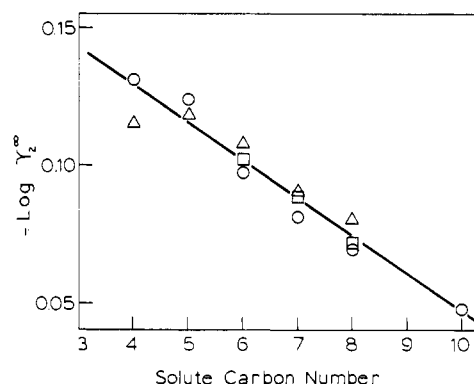


Figure 2. Plot of $-\log \gamma_2^\infty$ vs. solute carbon number for *n*-alkane solutes in *n*-tetracosane (*n*-C24) at 80°C

○ This work
 △ Young (45)
 □ Tewari et al. (42)

served in other similar systems and indicates that the athermal or entropic portion of the activity coefficient predominates; however, a detailed analysis of the data will be presented in a later publication.

Literature Cited

- (1) Bigli, C., Betti, A., Dondi, F., Francesconi, R., *J. Chromatogr.*, **42**, 176 (1969).
- (2) Bigli, C., Betti, A., Saglietto, G., Dondi, F., *ibid.*, **35**, 309 (1968).
- (3) Clark, R. K., Schmidt, H. H., *J. Phys. Chem.*, **69**, 3682 (1965).
- (4) Cruickshank, A. J. B., Everett, D. H., Westaway, M. T., *Trans. Faraday Soc.*, **61**, 235 (1965).
- (5) Cruickshank, A. J. B., Gainey, B. W., Young, C. L., *ibid.*, **64**, 337 (1968).
- (6) Cruickshank, A. J. B., Windsor, M. L., Young, C. L., *Proc. Royal Soc., Ser. A*, **295**, 259, 271 (1966).
- (7) Cruickshank, A. J. B., Windsor, M. L., Young, C. L., *Trans. Faraday Soc.*, **62**, 2341 (1966).
- (8) Desty, D. H., Swanton, W. T., *J. Phys. Chem.*, **65**, 766 (1961).
- (9) Dymond, J. H., Smith, E. B., "The Virial Coefficients of Gases," Clarendon Press, Oxford, England, 1969.
- (10) Eitre, L. S., *Anal. Chem.*, **36** (8), 31A (1964).
- (11) Evered, S., Pollard, F. H., *J. Chromatogr.*, **4**, 451 (1960).
- (12) Everett, D. H., *Trans. Faraday Soc.*, **61**, 1637 (1965).

- (13) Everett, D. H., Gaaney, G. W., Young, C. L., *ibid.*, **64**, 2667 (1968).
 (14) Everett, D. H., Stoddart, C. T. H., *ibid.*, **57**, 746 (1961).
 (15) Gaaney, B. W., Young, C. L., *ibid.*, **64**, 349 (1968).
 (16) Hammers, W. E., de Ligny, C. L., *Recueil*, **88**, 961 (1969).
 (17) Hammers, W. E., de Ligny, C. L., *ibid.*, **90**, 819 (1971).
 (18) Hammers, W. E., de Ligny, C. L., *ibid.*, p 912.
 (19) Hardy, C. J., *J. Chromatogr.*, **2**, 490 (1959).
 (20) Hicks, C. P., Young, C. L., *Trans. Faraday Soc.*, **64**, 2675 (1968).
 (21) James, A. T., Martin, A. J. P., *Biochem. J.*, **50**, 679 (1952).
 (22) James, M. R., Giddings, J. C., Keller, R. A., *J. Gas Chromatogr.*, **3**, 57 (1965).
 (23) Kováts, E., *Helv. Chim. Acta*, **41**, 1915 (1958).
 (24) Kudchadker, A. P., Alani, G. H., Zwolinski, B. J., *Chem. Rev.*, **68**, 659 (1969).
 (25) Langer, S. H., Johnson, B. M., Conder, J. R., *J. Phys. Chem.*, **72**, 4020 (1968).
 (26) Langer, S. H., Purnell, J. H., *ibid.*, **67**, 263 (1963).
 (27) Littlewood, A. B., Phillips, C. S. G., Price, D. T., *J. Chem. Soc.*, **1955**, p 1480.
 (28) Maffiolo, G., Lenoir, J. Y., Vidal, J., *Chim. Ind., Genie Chim.*, **104**, 1161 (1971).
 (29) Martin, R. L., *Anal. Chem.*, **33**, 347 (1961).
 (30) Martin, R. L., *ibid.*, **35**, 116 (1963).
 (31) Martire, D. E., Blasco, P. A., Carone, P. F., Chow, L. C., Vicini, H., *J. Phys. Chem.*, **72**, 3489 (1968).
 (32) Martire, D. E., Pollara, L. Z., *J. Chem. Eng. Data*, **10**, 40 (1965).
 (33) Martire, D. E., Riedl, P., *J. Phys. Chem.*, **72**, 3478 (1968).
 (34) McGlashan, M. L., Potter, D. J. B., *Proc. Roy. Soc., Ser. A.*, **267**, 478 (1962).
 (35) Meyer, E. F., *J. Chem. Educ.*, **50**, 191 (1973).
 (36) Meyer, E. F., Steck, K. S., Holte, R. D., *J. Phys. Chem.*, **77**, 2140 (1973).
 (37) Pease, E. C., Thorburn, S., *J. Chromatogr.*, **30**, 344 (1967).
 (38) Pecsar, R. E., Martin, J. J., *Anal. Chem.*, **38**, 1661 (1966).
 (39) Petsev, N., Dimitrov, C., *J. Chromatogr.*, **20**, 15 (1965); **23**, 382 (1966).
 (40) Sewell, P. A., Stock, R., *ibid.*, **50**, 10 (1970).
 (41) Snyder, P. S., Thomas, J. F., *J. Chem. Eng. Data*, **13**, 527 (1968).
 (42) Tewari, Y. B., Martire, D. E., Sheridan, J. P., *J. Phys. Chem.*, **74**, 2345 (1970).
 (43) Wicarova, O., Novak, J., Janak, J., *J. Chromatogr.*, **65**, 241 (1972).
 (44) Wilhoit, R. C., Zwolinski, B. J., "Handbook of Vapor Pressure and Heats of Vaporization of Hydrocarbons and Related Compounds," Thermodynamics Research Center, Texas A&M University, College Station, Tex., 1971.
 (45) Young, C. L., *Trans. Faraday Soc.*, **64**, 1537 (1968).

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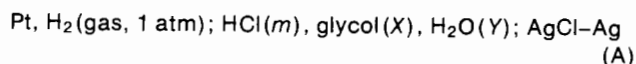
Activity Coefficients of Hydrochloric Acid in Several Ethylene Glycol-Water Mixtures from Emf Measurements

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From the electromotive force measurements of the cell of the type: Pt, H₂(gas, 1 atm); HCl(*m*), glycol(*X*), H₂O(*Y*); AgCl-Ag, the mean activity coefficients (γ^\pm) of HCl (up to *m* = 1) in several mixtures of ethylene glycol (*X*) and water (*Y*) (from 10 to 90 wt % glycol) are calculated using the standard potential (E°) values of the corresponding solvent mixtures reported earlier. As in the aqueous solutions, the activity coefficients pass through minima, but the minimum is relatively sharper with solution containing a higher percentage of glycol.

The standard potentials (E°) of the Ag-AgCl electrode in ethylene glycol and its several aqueous mixtures (10–90 wt %) at different temperatures (5–45°C) have been reported earlier from these laboratories (4). In the present work, these E° values have been used to calculate mean activity coefficients of hydrochloric acid in the glycol-water mixtures by extending the emf measurements of the cell



containing higher concentrations of HCl in solution (up to *m* = 1).

Experimental

Preparation of electrodes, purification of solvents and other experimental details, and the apparatus used were described elsewhere (4). All the emf readings were corrected to 1 atm pressure of hydrogen gas.

Results and Discussion

Activity coefficients (γ^\pm) have been calculated from the equation:

$$\log \gamma^\pm = \frac{E^\circ - E}{2k} - \log m \quad (1)$$

where *E* is the observed emf value of the cell (A) containing hydrochloric acid solution of molality *m*. Emf measurements were carried out at 25°C with all the glycol-water mixtures up to a concentration of 1*m*. For 50, 70, and 90% glycol-water mixtures, measurements were also conducted at 5° and 45°C. The emf values are shown in Table I. E° values of the Ag-AgCl electrode in different solvent mixtures (4) used in the calculation of the activity coefficients are at the top of the emf readings in the table.

For pure glycol at concentrations of HCl higher than 0.2*m*, steady emf readings were not obtained, and a tendency of the emf to increase with time was observed. The readings were not reported in the present work. No such difficulty, however, was observed in working with glycol water mixtures.

The values of γ^\pm at different temperatures were calculated from Equation 1 at the experimental molalities and plotted against log *m* on a large scale. From such plots, values of γ^\pm at rounded molalities were read off and are presented in Table II. Knight and coworkers (7, 3) have determined the mean activity coefficients of hydrochloric acid in ethylene glycol-water mixtures (up to 60%) at 25°C. Their reported values of γ^\pm of HCl appear to be slightly less (≈ 0.015) than the values obtained in this work. The figure shows the plot of γ^\pm against the corresponding molalities for various solvents at 25°C. All individual γ^\pm values for each emf reading for the solvent composition of *X* = 50 were plotted as a typical example.

The activity coefficients (γ^\pm) of HCl, which becomes unity at zero concentration of the electrolyte in the particular solvent under consideration, essentially constitute a measure of the interionic forces in the solvent and other effects dependent on the concentration of the solute in