Prediction of Binary Vapor-Liquid Equilibria

Members of a Homologous Series and a Common Solvent

DIMITRIOS TASSIOS[1] and MATTHEW VAN WINKLE
The University of Texas, Austin, Tex.

A method of predicting activity coefficients at infinite dilution in the binary systems consisting of a common solvent and the individual members of a homologous series from existing data on two of these binaries is presented. Since the activity coefficients at infinite dilution can be used in calculating the constants for any two constant equation relating activity coefficients and compositions (Van Laar, Margules, Wilson), activity coefficients for the whole concentration range for each binary can be estimated.

BECAUSE of the high cost of experimental investigation, it is desirable to develop methods to predict the behavior of mixtures under varying conditions from a minimum of experimental data. One area of interest is that related to extractive distillation wherein the selectivity of solvents for one of the components to be separated is an important factor in the selection of the optimum solvent for the process.

Numerous studies have been made and predictive methods developed requiring a minimum of only binary data, in some cases, to extensive mixture data in others. The basis for correlation varies widely, ranging from activity coefficient prediction at finite concentrations, infinite dilution activity coefficients, and selectivity ratios.

This investigation resulted in a predictive method for activity coefficients at infinite dilution in binary systems consisting of a common solvent and individual members of a homologous series from existing data on two binary systems in the series. The comparison of the activity coefficients at infinite dilution, of the individual members of the homologous series in the common solvent on the one hand, and of the common solvent in the members of the series on the other, is made under the same vapor pressure of the members. The method has been tested with activity coefficients reported in the literature (*6, 7, 8*) as well as the ones obtained experimentally in this investigation. The method was tested for a total number of eight systems with an average deviation of 1.1%.

Experimental data were obtained for the binary systems consisting of *p*-dioxane with *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, 1-pentene, 1-hexene, and 1-octene. All the data were obtained at constant temperature (80° C.).

EXPERIMENTAL

Materials. All the hydrocarbons used in this experimental work were obtained from the Phillips Petroleum Co. as the pure grade, 99.0 mole % minimum purity. The hydrocarbons were eluted through a 4-foot column packed with 10% UCON 1200 X on 80- to 100-mesh Diaport W in a GC-2A Beckmann gas chromatograph at its maximum

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[1] Present address: Newark College of Engineering, Newark, N. J.

Table I. Physical Properties of Materials (2)

	n-Alkanes				1-Alkenes			Solvent, *p*-Dioxane
	Hexane	Heptane	Octane	Nonane	Pentene	Hexene	Octene	
Molecular weight	86.17	100.20	114.22	128.25	70.13	84.16		
Vapor pressure (80.0° C.)								
Exptl.	1067.0	425.8	175.0	72.71		1251.9	203.95	380.4
Calcd.[a]	1068.3	427.77	175.04	72.71	3302.1	1252.7	203.92	378.8
Antoine constants								
A	6.87776	6.90240	6.42377	6.93513	6.84650	6.86572	6.93263	(*13*)
B	1171.53	1268.115	1355.126	1428.811	1044.9	1152.971	1353.5	
C	224.336	216.90	209.517	201.619	234.0	226.0	212.764	
Refractive index								
Exptl.	1.37244	1.38523	1.39536	1.40331	1.36853	1.38520	1.40653	1.41985
Lit.	1.37226	1.38511	1.39505	1.40311	1.36835	1.38502	1.40620	1.42020
Boiling point, 760 mm.								
Exptl.	68.75	...	125.61	...	...	...	...	101.10(*13*)
Lit.	68.74	98.43	125.67	150.80	27.97	63.49	121.28	101.22

[a] Using Antoine equation.

Table II. Constants for Chromatographic Calibration and Standard Deviations

System: *p*-Dioxane and	a_0	a_1	a_2	a_3	Standard Deviations
n-Hexane	−0.000512	0.081002	0.291269	−0.100911	2.5×10^{-6}
n-Heptane	−0.000247	0.716853	0.251255	0.032328	7.9×10^{-7}
n-Octane	−0.000206	0.653210	0.229184	0.117943	4.5×10^{-7}
n-Nonane	−0.000423	0.600908	0.198658	0.200070	1.9×10^{-6}
1-Pentene	0.000558	0.934639	0.115272	−0.049863	4.3×10^{-9}
1-Hexene	−0.000025	0.830379	0.299407	−0.130131	8.6×10^{-8}
1-Octene	−0.000009	0.663699	0.243039	0.093141	2.5×10^{-7}

sensitivity and exceeded 99.5 mole % purity. Other investigators (*3, 11*) have found the same results for the case of *n*-hexane and 1-hexene. The pure grade hydrocarbons were used without further purification. The alkenes were stored under an atmosphere of oxygen-free nitrogen in a cool place to minimize the formation of peroxides.

The reagent grade 1,4-dioxane was refluxed through silica gel, packed in a Soxhlet extraction unit, and then was distilled in a 3-foot by 3/4-inch vacuum jacketed glass column packed with glass helices at a reflux ratio of 20 to 1. The collection of the heart cut (middle 50 %) started when no impurities were observed in the distillate by eluting a sample through a 4-foot column packed with 10% UCON 1200 X on 80- to 100-mesh Diaport W.

Table III. Vapor-Liquid Equilibria Data

x_1	y_1	P_T, Mm.	γ_1	γ_2	ln γ_1/γ_2 Obsd.	ln γ_1/γ_2 Calcd.	Diff.
n-Hexane–*p*-Dioxane							
0.976	0.976	73.4	1.000	2.668	–0.981	–0.991	0.010
0.977	0.977	52.8	0.992	2.721	–1.009	–0.992	–0.017
0.902	0.914	69.6	1.009	2.351	–0.846	–0.859	0.014
0.751	0.819	33.8	1.057	1.890	–0.581	–0.573	–0.008
0.490	0.717	966.9	1.329	1.352	–0.016	–0.030	0.014
0.485	0.710	952.9	1.313	1.349	–0.027	–0.018	–0.009
0.408	0.681	915.7	1.442	1.243	0.149	0.156	–0.007
0.137	0.490	691.7	2.358	1.041	0.817	0.808	0.010
0.088	0.398	604.1	2.627	1.035	0.932	0.932	0.000
0.030	0.198	457.8	2.935	1.003	1.074	1.082	–0.009
0.074	0.363	587.1	2.767	1.048	0.971	0.968	0.003
n-Heptane–*p*-Dioxane							
0.017	0.063	400.1	3.508	1.003	1.252	1.228	0.024
0.049	0.152	435.7	3.172	1.017	1.138	1.130	0.007
0.079	0.209	458.1	2.817	1.018	1.018	1.040	–0.022
0.161	0.320	493.3	2.278	1.042	0.783	0.801	–0.019
0.353	0.451	529.7	1.575	1.170	0.297	0.294	0.004
0.515	0.518	542.5	1.257	1.384	–0.097	–0.083	–0.013
0.626	0.584	534.1	1.158	1.539	–0.284	–0.313	0.029
0.764	0.672	518.9	1.057	1.864	–0.567	–0.569	0.002
0.827	0.730	498.8	1.030	2.030	–0.678	–0.673	–0.005
0.852	0.759	492.4	1.026	2.092	–0.712	–0.712	–0.000
0.911	0.836	473.6	1.010	2.269	–0.809	–0.802	–0.007
0.977	0.951	445.4	1.009	2.464	–0.893	–0.894	0.001
n-Octane–*p*-Dioxane							
0.019	0.033	387.6	3.723	1.000	1.314	1.289	0.025
0.046	0.070	392.9	3.321	1.008	1.193	1.194	–0.001
0.119	0.137	398.9	2.575	1.029	0.917	0.948	–0.031
0.440	0.275	383.3	1.329	1.295	0.026	0.040	–0.014
0.494	0.301	375.8	1.271	1.360	–0.068	–0.086	0.018
0.770	0.468	306.1	1.045	1.871	–0.583	–0.594	0.011
0.885	0.633	253.7	1.015	2.135	–0.743	–0.743	–0.000
0.979	0.902	189.5	1.001	2.330	–0.845	–0.837	–0.008
n-Nonane–*p*-Dioxane							
0.987	0.875	83.9	1.008	2.182	–0.773	–0.751	–0.022
0.953	0.659	109.3	1.010	2.095	–0.730	–0.737	0.008
0.879	0.415	159.1	0.986	1.997	–0.706	–0.693	–0.012
0.769	0.277	217.1	1.051	1.814	–0.546	–0.590	0.045
0.316	0.111	341.4	1.585	1.176	0.299	0.317	–0.018
0.113	0.061	372.5	2.640	1.036	0.936	0.974	–0.038
0.027	0.021	381.9	3.820	1.003	1.338	1.300	0.038
1-Pentene–*p*-Dioxane							
0.062	0.485	718.8	1.885	1.006	0.628	0.631	–0.003
0.093	0.583	863.5	1.820	1.005	0.594	0.576	0.018
0.104	0.601	910.5	1.774	1.034	0.540	0.557	–0.017
0.142	0.671	73.8	1.702	1.042	0.490	0.489	0.002
1-Hexene–*p*-Dioxane							
0.885	0.930	94.8	1.007	1.797	–0.579	–0.590	0.011
0.742	0.855	15.0	1.045	1.575	–0.410	–0.393	–0.018
0.489	0.745	992.1	1.228	1.248	–0.016	–0.018	0.003
0.285	0.629	819.9	1.488	1.088	0.313	0.310	0.003
0.108	0.415	602.2	1.920	1.024	0.629	0.613	0.017
0.058	0.277	504.4	2.020	1.010	0.693	0.702	–0.009
0.015	0.095	416.1	2.196	1.014	0.772	0.779	–0.006
1-Octene–*p*-Dioxane							
0.063	0.080	389.9	2.393	1.013	0.859	0.848	0.011
0.134	0.142	399.0	2.038	1.043	0.670	0.671	–0.002
0.240	0.207	399.2	1.660	1.099	0.413	0.426	–0.013
0.397	0.285	383.3	1.316	1.191	0.099	0.107	–0.008
0.575	0.382	356.1	1.132	1.354	–0.180	–0.187	0.007
0.716	0.491	321.7	1.058	1.510	–0.356	–0.372	0.016
0.880	0.698	262.8	1.012	1.742	–0.544	–0.533	–0.011

Table I summarizes some of the physical properties of the materials used.

Apparatus and Procedure. A modified Colburn still, previously described (*11*), was used in the determination of the vapor-liquid equilibrium data. A ballast tank, consisting of a 1.5-liter copper coil immersed in a constant temperature oil bath, was used to smooth pressure fluctuations caused by changes in the ambient temperature. Temperatures were measured by means of a copper-constantan thermocouple, precalibrated against a set of U.S. National Bureau of Standards calibrated mercury-in-glass thermometers, and a Universal K-3 Leeds and Northrup potentiometer. The pressure in the still was measured by means of an absolute mercury-in-glass manometer read with the use of a cathetometer. The temperature of the boiling liquid was set at 80.0° ± 0.8° C. by proper adjustment of the pressure.

Gas chromatography utilizing a Beckman GC-2A gas chromatograph (Model 17302) was used for the analysis of the liquid and vapor phases. In order that all changes in the instrument sensitivity are normalized and minimized, area fractions instead of absolute areas were used for calibration. The following dependence of the mole fraction, MF, on the observed area fraction, AF, was used:

$$MF = a_0 + a_1AF + a_2AF^2 + a_3AF^3 \tag{1}$$

The constants a_0, a_1, a_2, and a_3 were obtained by a least squares fit through 11 to 15 points for each binary system. The values for these constants with the obtained standard deviations are presented in Table II.

RESULTS

The activity coefficient of component i in a binary system is given by the following equation, assuming the vapor phase to be an ideal solution of real gases (*12*)

$$\ln \gamma_i = \ln \frac{y_iP}{x_iP_i^0} + \frac{(P - P_i^0)}{RT}(B_{ii} - V_i^L) \tag{2}$$

Values for the function $(B_{ii} - V_i^L)$ for n-alkanes and 1-alkenes are reported by Hanson (*3*). Values for the same function for the case of p-dioxane were obtained from data reported by Vincon and Martin (*13*).

The results were tested for thermodynamic consistency by using the area test. According to Van Ness (*12*) the following relation must hold for isothermal data.

$$\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2}\, dx_1 = -\int_{x_1=0}^{x_1=1} \frac{\Delta V}{RT} \frac{dP}{dx_1}\, dx_1 \tag{3}$$

The integrand is generally negligible (*12*) and a plot of ln (γ_1/γ_2) *vs.* x_1 should yield two areas, one above and one below the x axis, that are equal if the data are consistent.

The integral in Equation 3 was evaluated numerically by the use of a computer employing the following empirical relation between ln (γ_1/γ_2) and x_1:

$$\ln(\gamma_1/\gamma_2) = A_0 + A_1(x_1 - 0.5) + A_2(x_1 - 0.5)^2 \tag{4}$$

The constants A_0, A_1, and A_2 were determined by means of a least squares fit through the experimental values at ln (γ_1/γ_2). A "consistency index", defined by Hanson (*3*) as

$$\text{C.I.} = \frac{Ip + In}{|Ip| + |In|} \tag{5}$$

where Ip = positive area, and In = negative area, was used to express the consistency of the data.

Table III presents the experimental vapor-liquid equilibrium data for the systems studied. It also includes the activity coefficients, the values of the function ln (γ_1/γ_2), observed and calculated using Equation 4. The values of the consistency index for the systems studied are presented in Table IV. Activity coefficients at infinite dilution were calculated from Equation 4 as follows:

$$\ln \gamma_1^0 = \left(\ln \frac{\gamma_1}{\gamma_2}\right)_{x_1=0} = A_0 - \frac{A_1}{2} + \frac{A_2}{4} \tag{6a}$$

$$-\ln \gamma_2^0 = \left(\ln \frac{\gamma_1}{\gamma_2}\right)_{x_1=1} = A_0 + \frac{A_1}{2} + \frac{A_2}{4} \tag{6b}$$

The vapor-liquid equilibrium data were tested for thermodynamic consistency by plotting ln γ_1/γ_2 *vs.* x, and comparing the areas above and below ln $\gamma_1/\gamma_2 = 0$, and all systems were consistent within the estimated limits of experimental error. Figure 1 presents a plot at ln(γ_1/γ_2) *vs.* x_1 for the binary system p-dioxane–1-pentene to show how γ^0 of pentene was evaluated. Only the low concentration range of pentene was studied, to avoid the necessity for operation of the glass equipment at super atmospheric pressures.

Proposed Method. Prediction of activity coefficients at infinite dilution of the individual members of a homologous series in a common solvent has been studied by Pierotti, Deal, and Derr (*9*) and by Black, Derr, and Papodopoulos (*1*). The method relates the activity coefficients at infinite dilution to the number of carbon atoms of the solute and solvent. A different approach to the problem, although still empirical in nature, is presented here. This method was developed by comparing the activity coefficients of the individual members of a homologous series at infinite dilution in a common solvent and the infinite dilution activity coefficient of the solvent in the members of the series under the same total pressure and temperature, taking into account the difference in vapor pressure of the members

Table IV. Consistency Index

System: Dioxane and	C.I.
n-Hexane	−0.012
n-Heptane	0.026
n-Octane	0.018
n-Nonane	0.012
1-Hexene	−0.012
1-Octene	0.019

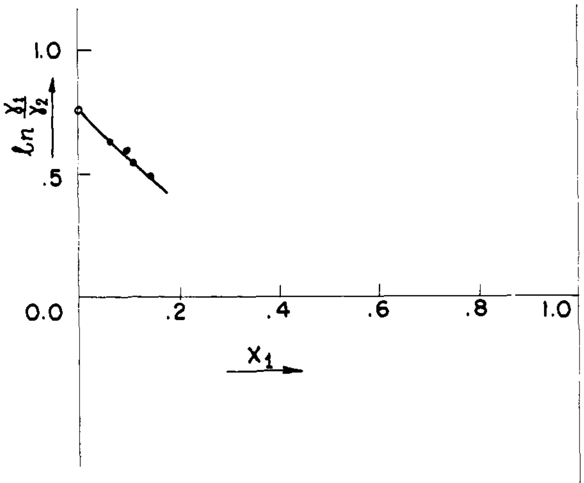

Figure 1. Determination of γ^0 for 1-pentene in dioxane–1-pentene system

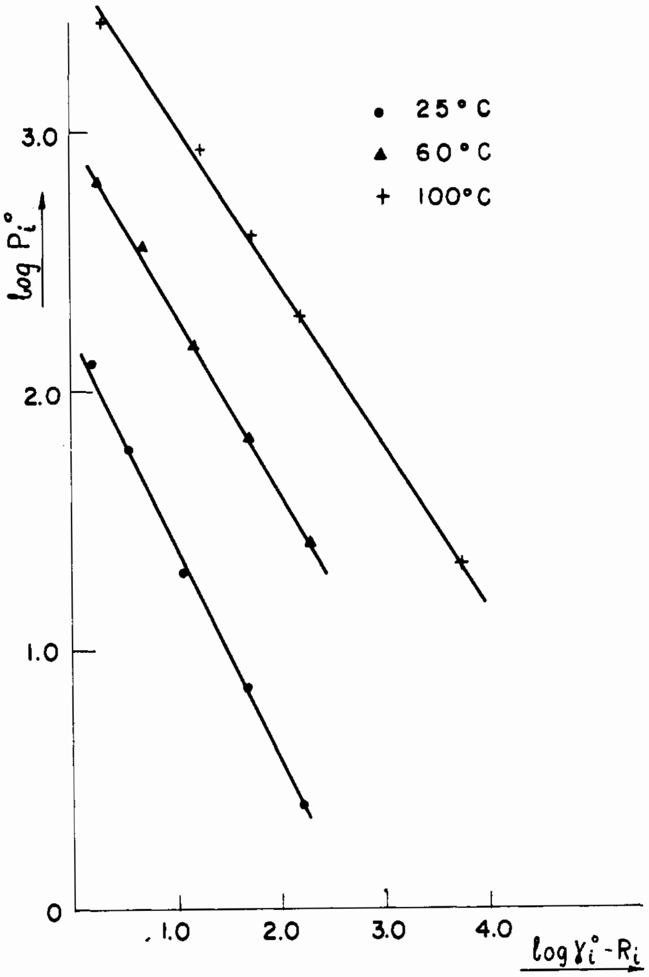

Figure 2. Correlation of infinite dilution activity coefficients—*n*-alcohols and water

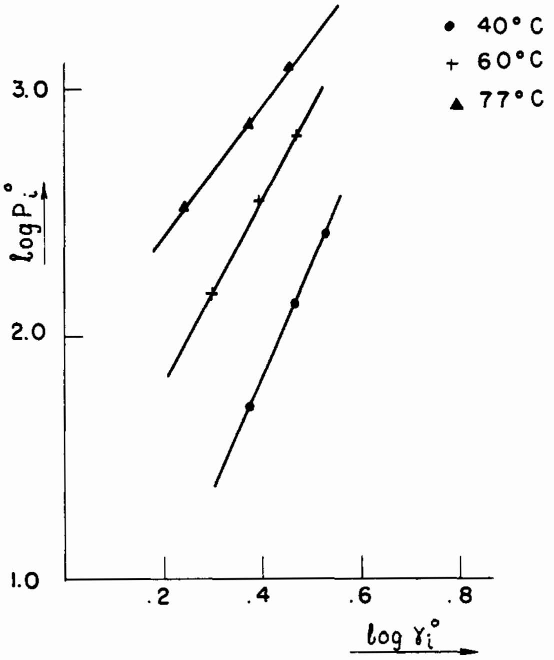

Figure 3. Correlation of infinite dilution activity coefficients —*n*-alcohols–ethyl acetate

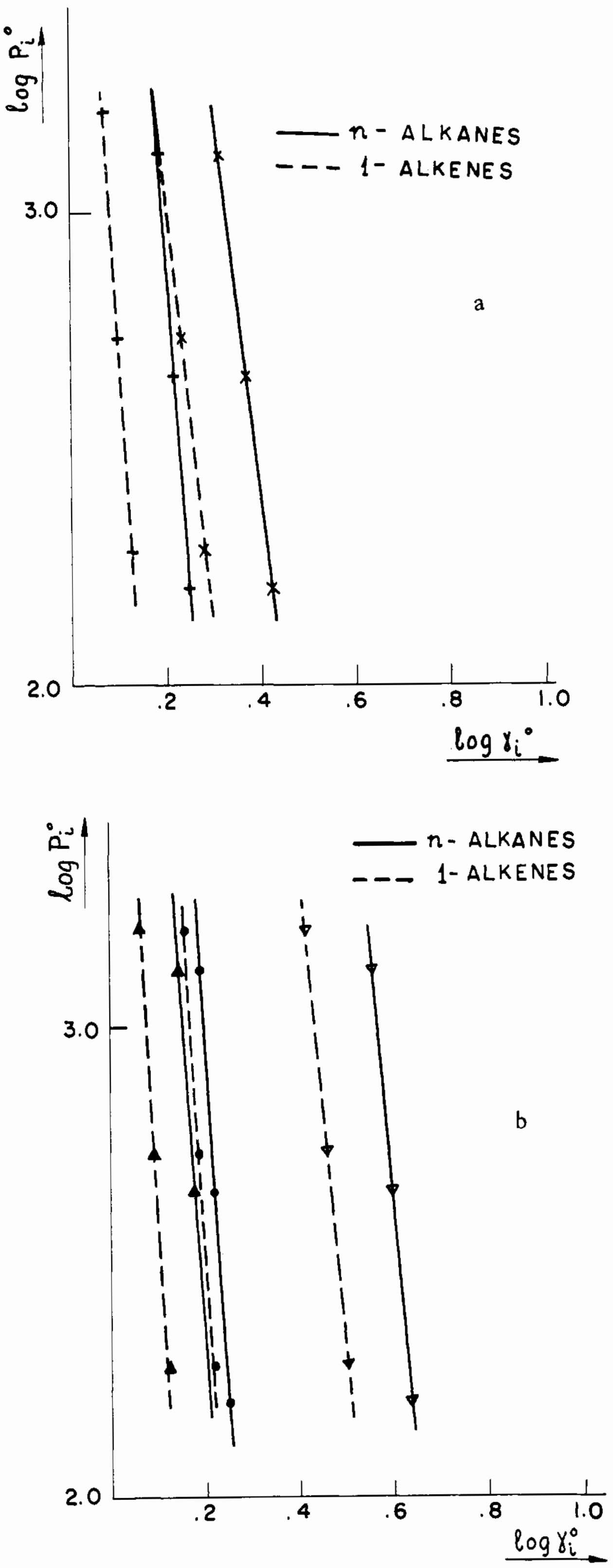

Figure 4. Correlation of infinite dilution activity coefficients

a. 1-Alkenes, *n*-alkanes and (X) di-*n*-butyl phthalate, (+) di-*n*-butyl tetrachlorophthalate

b. Alkenes, *n*-alkanes, (●) 1-hexadecanol, (▲) *N,N*-dimethylmyristamide, (▼) benzyl diphenyl of the series at the temperature. A similar idea was presented by Hildebrand and Scott (*4*) who noted that, "In comparing the attraction of the solvent for different solutes it is necessary to take into account differences in vapor pressures of the different solute liquids, for a liquid at lower vapor pressure will be less soluble than one at higher vapor pressure, other things being equal."

At low pressure, the activity coefficient of the member i of the series at infinite dilution in the solvent s can be found by taking the limits of both sides of Equation 2 as x approaches zero:

$$\ln \gamma_i^0 = \frac{P_s^0 - P_i^0}{RT} (B_{ii} - V_i^L) + \ln \left[\left(\frac{y}{x}\right)_i^0 \left(\frac{P_s^0}{P_i^0}\right) \right] \tag{7}$$

where:

$$\left(\frac{y}{x}\right)_i^0 = \lim_{x_i \to 0} \left(\frac{y}{x_i}\right)$$

In order for $(y/x)_i^0$ to be explicitly related to P_i^0, for a given pressure and temperature, the assumption is made that

$$(y/x)_i^0 = L(P_i^0)^c \tag{8}$$

where L and c are constants depending on homologous series, solvent, and temperature but independent of the member of the homologous series.

Substituting Equation 8 into Equation 7, the following expression is obtained:

$$\ln \gamma_i^0 - \frac{P_s^0 - P_i^0}{RT} (B_{ii} - V_i^L) = C_0 + (c - 1) \ln P_i^0 \tag{9}$$

where

$$C_0 = \ln (L)\ (P) \tag{10}$$

If Equation 9 is arranged in the form:

$$\ln \gamma_i^0 - \frac{P_s^0 - P_i^0}{RT} (B_{ii} - V_i^L) - (C - 1) \ln P_i^0 = C_0 \tag{9a}$$

it is implied that for a given temperature, the nonideality of the members of a homologous series in a common solvent at infinite dilution is the same, provided correction for the difference in vapor pressures is made. This substantiated the statement of Hildebrand and Scott (*4*).

A similar hypothesis can be made relating the ratio $(y/x)^0$ of the solvent at infinite dilution in each of the members of the homologous series to the vapor pressure of each of the members of the series.

$$(y/x)_s^0 = L' (P_i^0)^{c'} \tag{11}$$

where L' and c' have the same meaning as L and c. Under these conditions the following expression for the activity coefficient at infinite dilution of the solvent in each of the members of the homologous series is obtained:

$$\ln \gamma_s^0 - \frac{P_i^0 - P_s^0}{RT} (B_{ss} - V_s^L) = C_0' + (c' + 1) \ln P_i^0 \tag{12}$$

where

$$C_0' = \ln (L'/P_s^0) \tag{13}$$

The following notation will be used hereafter:

$$R_i = \frac{(P_s^0 - P_i^0)}{RT} (B_{ii} - V_i^L) \tag{14}$$

$$R_s = \frac{(P_i^0 - P_s^0)}{RT} (B_{ss} - V_s^L) \tag{14a}$$

If the assumption is valid, a plot of $(\ln \gamma_k^0 - R_k)$, $k = s$ or i, *vs.* $\ln P_i^0$ should yield a straight line. If the activity coefficients at infinite dilution are from experimental activity coefficients that were not corrected for vapor phase imperfections, $R = 0$ and $\ln \gamma_k^0$ *vs.* $\ln P_i^0$ must be plotted.

Test of the Method. The method was first tested for the systems *n*-alcohols in water. Activity coefficients at infinite dilution which were obtained by extrapolation of measured activity coefficient data in the low concentration range are reported by Pierroti, Deal, and Derr (*8*). No meaningful thermodynamic consistency test could be applied to them. Values for the function $(B - V^L)$ for the *n*-alcohols are reported by Hanson (*3*) based on the data reported in the literature (*5, 14*). The second virial coefficient for water was taken from Rowlinson (*10*). The data, for three different temperatures, are plotted in Figure 2.

Activity coefficients at infinite dilution for the binaries, ethyl acetate with methanol, ethanol, and 1-propanol at 760 mm. reported by Murti and Van Winkle (*7*), were also used to test the method. The experimental activity coefficients were not corrected for vapor phase imperfections. Since the data were obtained under constant pressure only, the activity coefficients of the alcohols at infinite dilution in ethyl acetate can be considered as those evaluated at the same temperature, namely the boiling point temperature of ethyl acetate at 760 mm. (77.2° C.). The data are plotted on Figure 3. Data for two more temperatures, 60° and 40° C., are also presented on the same figure.

Activity coefficients at infinite dilution of three 1-alkenes, pentene, hexene, and heptene and the corresponding

Table V. Activity Coefficients of Infinite Dilution and Related Functions for the Systems

Hydrocarbon	*VP*	log *VP*	γ_i^0	log γ_i^0	R_i	log $\gamma_i^0 - R_i$	γ_s^0	log γ_s^0	R_s	log $\gamma_s^0 - R_s$
					n-Alkanes–*p*-Dioxane					
n-C_6	1068.3	3.02869	3.212	0.507	+0.019	0.488	2.799	0.447	−0.023	0.470
n-C_7	425.8	2.62921	3.543	0.550	+0.002	0.548	2.531	0.403	−0.003	0.406
n-C_8	175.0	2.24305	3.812	0.582	−0.011	0.593	2.346	0.376	+0.007	0.369
n-C_9	72.7	1.86143	3.916	0.593	−0.021	0.614	2.129	0.327	+0.010	0.317
					1-Alkenes–*p*-Dioxane					
1-Pentene	3302.2	3.519	2.120	0.327	0.051	0.276	. . .	. . .	. . .	. . .
1-Hexene	1252.7	3.099	2.254	0.353	0.022	0.331	2.108	0.325	−0.029	0.354
1-Octene	203.95	2.310	2.736	0.437	−0.008	0.445	1.844	0.268	+0.005	0.263

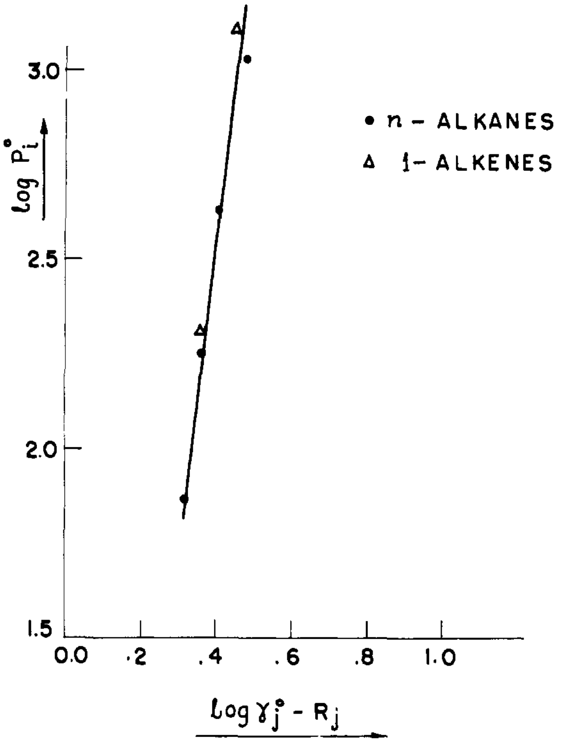

Figure 5. Correlation of infinite dilution activity coefficients—1-alkenes, *n*-alkanes, in p-dioxane

n-alkanes in five different solvents, 1-hexadecanol, *N,N*-dimethyl myristamide, di-*n*-butyl tetrachlorophthalate, di-*n*-butyl phthalate, and benzyl diphenyl, are reported by Martire and Pollare (*6*). They were obtained by direct application of gas-liquid chromatography in measuring activity coefficients at infinite dilution. The data are successfully correlated by this method (Figure 4,*a*, 4,*b*).

Activity coefficients at infinite dilution, obtained in this study, and some related functions, are presented in Table V. The results are plotted in Figures 5 and 6.

Table VI presents the values of the constants in Equations 9 and 12 obtained in the correlation of all of the

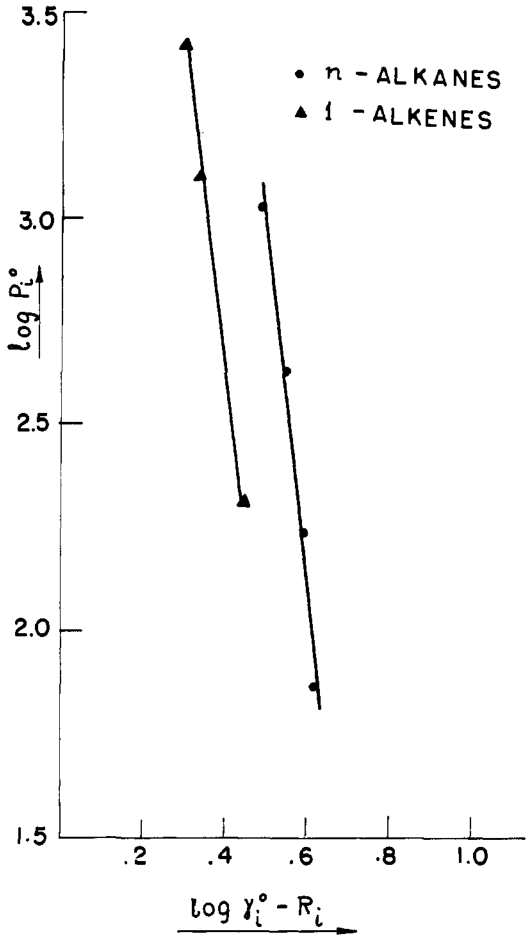

Figure 6. Correlation of infinite dilution activity coefficients—*p*-dioxane in *n*-alkanes, 1-alkenes

Table VI. Correlation of Activity Coefficients at Infinite Dilution for Eight Different Systems with the Proposed Method

Solvent[a]	Solute	*T*	C_0	*c*	Slope	Maximum Dev., % γ^0	Maximum Dev., % log γ^0	Av. Dev., % γ^0	Av. Dev., % log γ^0
Water	*n*-Alcohols	25	2.708	−0.219	−1.219	12.2	17.6	5.8	5.1
Water	*n*-Alcohols	60	4.329	−0.450	−1.450	4.2	2.4	2.2	1.1
Water	*n*-Alcohols	100	6.011	−0.651	−1.651	14.6	17.2	8.4	5.2
Et. Acet.	*n*-Alcohols	40	0.036	1.197	0.197	0.4	0.5	0.3	0.3
Et. Acet.	*n*-Alcohols	60	−0.277	1.265	0.265				
Et. Acet.	*n*-Alcohols	77	−0.751	1.392	0.392	0.3	0.4	0.2	0.2
A	*n*-Alkanes	53.2	0.362	0.933	−0.067	0.1	0.3	0.1	0.2
A	1-Alkenes	53.2	0.357	0.937	−0.063	0.2	0.4	0.1	0.2
B	*n*-Alkanes	53.2	0.333	0.934	−0.066	0.5	1.3	0.3	0.8
B	1-Alkenes	53.2	0.256	0.942	−0.058	0.3	1.2	0.2	0.8
C	*n*-Alkanes	53.2	0.374	0.952	−0.068	0.1	0.3	0.1	0.2
C	1-Alkenes	53.2	0.306	0.922	−0.078	0.5	2.4	0.3	1.7
D	*n*-Alkanes	53.2	0.713	0.916	−0.084	0.0	0.0	0.0	0.0
D	1-Alkenes	53.2	0.694	0.913	−0.087	0.6	0.6	0.3	0.3
E	*n*-Alkanes	53.2	0.625	0.891	−0.109	0.1	0.1	0.1	0.1
E	1-Alkenes	53.2	0.529	0.892	−0.108	0.0	0.0	0.0	0.0
p-Dioxane	*n*-Alkanes	80.0	0.826	0.891	−0.109	2.4	1.8	2.1	1.6
p-Dioxane	1-Alkenes	80.0	0.741	0.859	−0.141	0.5	0.5	0.3	0.4
n-Alkanes	*p*-Dioxane	80.0	0.110	−0.891	0.109	3.0	3.5	1.5	1.7
1-Alkenes	*p*-Dioxane	80.0	-0.009	−0.883	0.117	0.0	0.0	0.0	0.0
n-Alkanes and 1-Alkenes	*p*-Dioxane	80.0	0.110	−0.904	0.096	18.2	27.4	10.0	12.6

[a] A = 1-Hexadecanol. *B* = *N,N*-Dimethyl myristamide. *C* = Di-*n*-butyl tetrachlorophthalate. *D* = Di-*n*-butyl phthalate. *E* = Benzyl diphenyl.

presented sets of experimental data. A least squares fit was employed in this calculation.

DISCUSSION

Because of the relatively small deviations of the calculated from the observed activity coefficients, the authors concluded that the proposed method successfully correlates the experimental data. With the exception of the system water–*n*-alcohols, where the maximum deviation is 17.4%, for the rest of the systems, the maximum deviation is below 3% and in most cases below 1%. The maximum deviation in the case of the systems water–*n*-alcohols occurs in methanol and is due mainly to the very low value of the logarithm of the activity coefficient at infinite dilution of methanol in water (0.184). The calculated value is 0.152. So, while the absolute error is small, the relative one is fairly large.

The behavior of the homologous series *n*-alkane and 1-alkene in a common solvent presents a rather interesting characteristic. The slopes of the line are very close. This suggests that once the behavior of one of the series with some solvent is known, one experimental point suffices within certain limits to establish the behavior of the other series. Furthermore, it shows that if a solvent enhances the relative volatility for a pair of *n*-alkanes, and 1-alkene, with the same number of carbon atoms, it will have the same effect on any other pair. Whether this applies to any two homologous series that differ only by a double bond, is to be decided by further experimentation.

NOMENCLATURE

a_0, a_1, a_2, etc. = constants
A_0, A_1, A_2, etc. = constants
AF = area fraction
B_{ii} = second virial coefficient
c, c' = constants
C.I. = consistency index
Ip, In = positive part, negative part of integral, Equation 3
L, L' = constants
MF = mole fraction
P_i° = vapor pressure, component i
P = total pressure
R = gas law constant
T = absolute temperature
V_i^L = molal liquid volume, component i
x, y = mole fractions
γ = activity coefficient
Δ = difference

LITERATURE CITED

(1) Black, C., Derr, E.L., Papodopoulos, M.N., *Ind. Eng. Chem.* **55**, 8, 40 (1963).
(2) Dreisbach, R.R., *Advan. Chem. Ser.* No. **22** (1959).
(3) Hanson, D.O., Ph.D. dissertation, University of Texas, Austin, Tex., 1965.
(4) Hildebrand, J.H., Scott, R.L., "The Solubility of Non-Electrolytes," 3rd ed., p. 173, Reinhold, New York, 1954.
(5) Kretschmer, C.B., Wiebe, R., *J. Am. Chem. Soc.* **76**, 2579 (1954).
(6) Martire, D.E., Pollara, L.Z., J. CHEM. ENG. DATA **10**, 40 (1965).
(7) Murti, P.J., Van Winkle, M., CHEM. ENG. DATA SER. **3**, 1, 72 (1958).
(8) Pierotti, G.J., Document 5782, American Documentation Institute, Washington, D. C., 1958.
(9) Pierotti, G.J., Deal, C.A., Derr, E.L., *Ind. Eng. Chem.* **51**, 95 (1959).
(10) Rowlinson, J.S., *Trans. Faraday Soc.* **45**, 974 (1949).
(11) Suryanarayana, Y.S., Ph.D. dissertation, University of Texas, Austin, Tex., 1965.
(12) Van Ness, H.C., "Classical Thermodynamics of Non-Electrolyte Solutions," p. 131, Macmillan Co., New York, 1964.
(13) Vinson, C.G., Jr., Martin, J.J., J. CHEM. ENG. DATA **8**, 74 (1963).
(14) Williamson, K.D., Ph.D. dissertation, University of Texas, Austin, Tex., 1954.

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