Table V. Standard Deviation of Eq 3 (σ_V), 4 (σ_α), and 5 (σ_η), Concerning the Different Mixtures

x_1	$10^6\sigma_V$	$10^4\sigma_\alpha$	σ_η
0.0	0.2	0.01	
0.0503			0.02
0.2024	0.2	0.005	
0.2004			0.03
0.4002	0.3	0.01	
0.3998			0.09
0.6606	0.3	0.01	
0.6335			0.05
0.8064	0.7	0.03	
0.7999			0.04
1.0	0.03	0.002	0.04

molar volumes vs. x_1 (Figure 1) points out the constancy of the molar volumes in the complete concentration range. The volume coefficient of expansion, α, shows a positive deviation from simple additivity and is roughly constant in the composition range $0.2 < x_2 < 1$ and is decreasing in the range $x_2 < 0.2$ (Figure 1). The activation energy $E = R\,\partial \ln \eta/\partial(1/T)$ of viscous flow for the mixtures agrees satisfactorily with the corresponding value for octadecanoic acid previously reported (*3*) (Figure 1). The plot E vs. x_2 shows a negative deviation from additivity.

Acknowledgment

Thanks are due to V. Amici and G. Cardarelli for technical assistance.

Glossary

α	volume coefficient of thermal expansion
d	density
E	activation energy
η	viscosity
ν	line frequency
T	absolute temperature
t	Celsius temperature
V	volume
V_m	mean volume per mixture mole
V_{exptl}	experimental volume
V_{calcd}	calculated volume
$\bar{V}_i$	partial molar volume of the *i*th component
x_i	molar fraction of the *i*th component
ω	angular speed of rotation of the internal cylinder
$W^{\text{bob}}_{\text{air,melt}}$	weight fo the bob in the air or in the melt, respectively

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Isothermal Compressibility of Cyclohexane–*n*-Decane, Cyclohexane–*n*-Dodecane, and Cyclohexane–*n*-Tetradecane

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Isothermal compressibilities for the binary mixtures of cyclohexane–*n*-decane, cyclohexane–*n*-dodecane, and cyclohexane–*n*-tetradecane have been measured at 298.15, 308.15, 318.15, and 333.15 K. The calculated "excess" function κ_T^E is positive for the three mixtures, having its maximum at or around $x_1 = 0.5$.

Introduction

In a previous paper (*1*) we published our experimental results on the isothermal compressibility of binary systems consisting of cyclohexane–*n*-hexane, –*n*-heptane, –*n*-octane, and –*n*-nonane. Here we present similar measurements on another set of binary mixtures of cyclohexane with *n*-alkanes, namely, *n*-decane, *n*-dodecane, and *n*-tetradecane. The purpose is to round out this type of experimental result on a set of systems for which we already have data on excess enthalpy (*2*) and excess volume (*3*).

Experimental Section

The liquid isothermal compressibility, defined as

$$\kappa_T = -V^{-1}(\partial V/\partial p)_T \tag{1}$$

has been determined by using a direct-measurement piezometric method. The details of this technique were described in depth in previous papers (*4*–*6*). It allows individual measurements with errors below 0.5%.

The liquid volume involved in compressibility determination is calculated from its weight and density. Therefore we measured this for the pure substances at the four temperatures at which this work was carried out. In Table I we report the chemical source, the research grade claimed by the manufacturer, and the experimental density values obtained by us. For comparison sake, literature (*7*) values at 298.15 K are shown in the last column.

The mercury purification procedure has been described in a previous paper (*6*).

As usual the volume of a mixture is expressed by eq 2,

$$V = x_1V_1 + x_2V_2 + V^E \tag{2}$$

where the excess volume V^E has to be systematically measured. The cyclohexane–*n*-dodecane system at 288.15, 298.15, and 308.15 K was done by Gómez and Liu (*8*), who found no change with temperature; but their values at 298.15 K were slightly lower than those reported by Sânchez and Núñez (*3*). These authors measured V^E for the whole set of

0021-9568/81/1726-0022$01.00/0

Table I. Experimental Densities ρ at Various Temperatures and Comparison with Literature Data at 298.15 K and Mole Fraction Purity (x) of the Liquids

			ρ/(g cm^{-3})				
			exptl				lit.[a]
compd	source	10^2x	298.15 K	308.15 K	318.15 K	333.15 K	298.15 K
cyclohexane	Merck z.a.	⩾99.5	0.773 92	0.764 43	0.754 71	0.740 11	0.773 89
n-decane	Fluka purum	⩾99	0.726 37	0.718 92	0.711 29	0.699 56	0.726 25
n-dodecane	Fluka purum	⩾99	0.745 19	0.737 97	0.730 67	0.719 72	0.745 16
n-tetradecane	Fluka puriss	⩾99	0.759 18	0.752 12	0.745 06	0.734 50	0.759 30

[a] Reference 7.

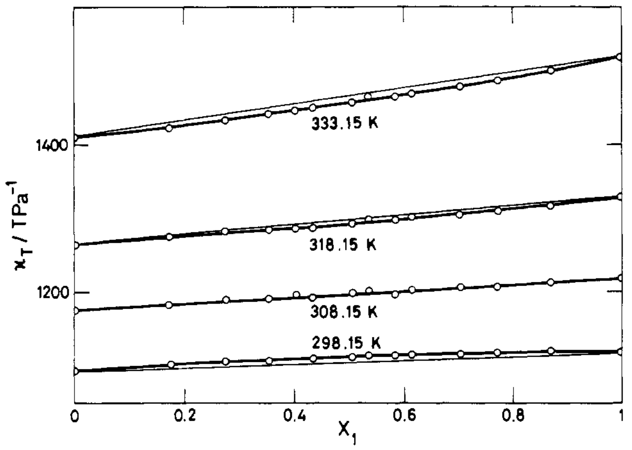

Figure 1. Isothermal compressibility κ_T vs. cyclohexane mole fraction x_1 for the cyclohexane–*n*-decane system.

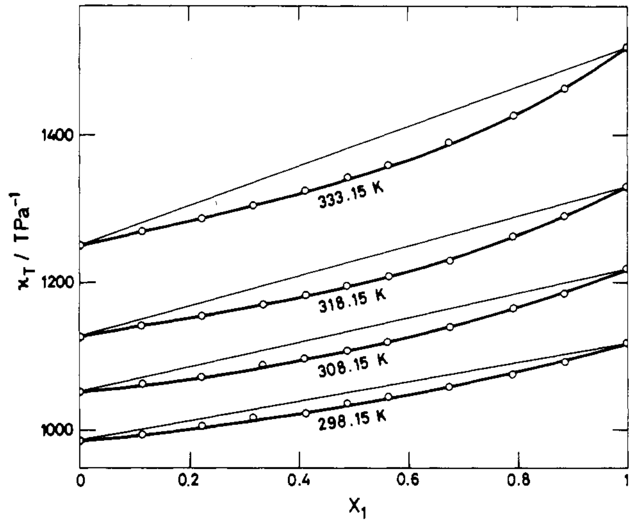

Figure 2. Isothermal compressibility κ_T vs. cyclohexane mole fraction x_1 for the cyclohexane–*n*-dodecane system.

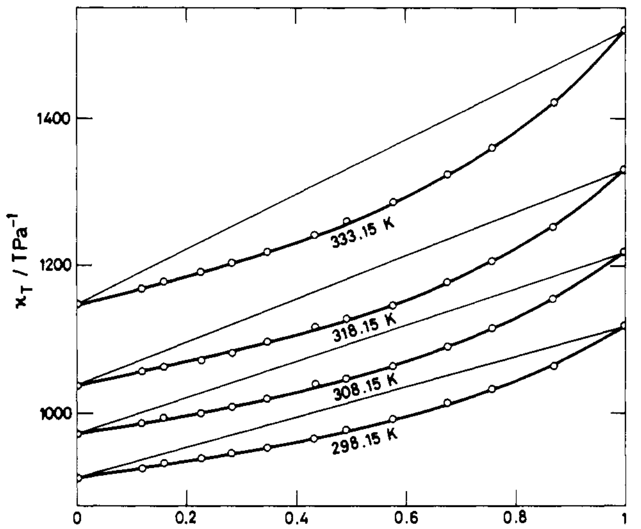

Figure 3. Isothermal compressibility κ_T vs. cyclohexane mole fraction x_1 for the cyclohexane–*n*-tetradecane system.

binary systems consisting of cyclohexane with one of the even *n*-alkanes going from *n*-hexane to *n*-hexadecane. Because of the small values for V^E, the applied isothermal compressibility correction for these systems is always lower than 0.4%. For this reason we have accepted as valid the data of Sânchez and Nũñez (*3*) and have also assumed that V^E is independent of temperature for the three systems.

Results and Discussion

The isothermal compressibility of cyclohexane–*n*-decane, cyclohexane–*n*-dodecane, and cyclohexane–*n*-tetradecane was determined for the whole mole composition range at negligible pressures and at 298.15, 308.15, 318.15, and 333.15 K. Measurements on the pure substances were run in duplicate, and the results compared with those in the literature (*1*, *6*). Experimental values for κ_T at the various mole fractions are given in Table II. For all systems the data were fitted as a function of the cyclohexane mole fraction, x_1, to a polynomial equation of the type

$$\kappa_T/\mathrm{TPa}^{-1} = \sum_{i=0} A_i x_1^{\,i} \qquad (3)$$

The coefficients A_i and the standard deviations σ are shown in Table III.

The values of κ_T have been plotted as a function of the cyclohexane mole fraction in Figures 1-3. The solid-line curves are for the mixture κ_T values obtained through eq 3. Also in the same figures we observe that, for all three systems and at any mole fraction, κ_T increases with temperature. For the cyclohexane–*n*-decane system we notice in Figure 1 at 298.15 K that the experimental solid-line curve falls below the straight line joining the pure-substance κ_T; but at 308.15 K the curve and the straight line coincide. At the remaining temperatures for this system and at all four temperatures for the other two systems, cyclohexane–*n*-dodecane and cyclohexane–*n*-tetradecane, the experimental curves are farther below the corresponding straight line the higher the temperature and the longer the *n*-alkane chain length. However, the deviation of the curve from the straight line is not an excess function since the straight line does not correspond to the ideal system.

Differentiating eq 2 with respect to pressure at constant temperature, we find by proper rearrangement

$$(\partial V^E/\partial p)_T = (\partial V/\partial p)_T - x_1(\partial V_1/\partial p)_T - x_2(\partial V_2/\partial p)_T \qquad (4)$$

where $(\partial V^E/\partial p)_T$ is itself an excess function and represents the difference of the corresponding values for the real system and the ideal one. Some authors (*9*) prefer to deal with this excess function in their solution studies. We have calculated it for all mole fractions investigated in the three systems. The data

Table II. Experimental Values of Isothermal Compressibility κ_T, κ_T^E, and $(\partial V^E/\partial p)_T$ at Negligible Pressures

x_1	κ_T/ TPa^{-1}	κ_T^E/ TPa^{-1}	$10^{-3}(\partial V^E/\partial p)_T$/ ($cm^3\ mol^{-1}\ TPa^{-1}$)	κ_T/ TPa^{-1}	κ_T^E/ TPa^{-1}	$10^{-3}(\partial V^E/\partial p)_T$/ ($cm^3\ mol^{-1}\ TPa^{-1}$)
			Cyclohexane (1)–*n*-Decane (2)			
		T = 298.15 K			T = 318.15 K	
0	1095	0	0	1265	0	0
0.1732	1102	6	−1.0	1276	6	−1.1
0.2769	1105	8	−0.9	1282	8	−1.4
0.3545	1107	9	−1.4	1286	9	−1.4
0.4042				1288	8	−1.3
0.4350	1110	11	−1.7	1288	7	−1.1
0.5070	1113	13	−1.4	1294	9	−1.4
0.5360	1115	14	−2.1	1300	13	−2.1
0.5852	1114	12	−1.7	1299	10	−1.4
0.6162	1114	11	−1.6	1303	11	−1.6
0.7044	1115	10	−1.3	1305	7	−1.1
0.7722	1116	9	−1.1	1311	7	−0.9
0.8691	1119	8	−0.9	1317	4	−0.4
1	1120	0	0	1331	0	0
		T = 308.15 K			T = 333.15 K	
0	1176	0	0	1411	0	0
0.1732	1183	4	−0.7	1424	3	−0.6
0.2769	1190	8	−1.5	1435	7	−1.3
0.3545	1191	8	−1.2	1443	9	−1.6
0.4042	1198	14	−2.2	1448	10	−1.7
0.4350	1194	8	−1.3	1451	11	−1.8
0.5070	1201	13	−1.9	1459	12	−2.0
0.5360	1201	12	−1.8	1466	16	−2.6
0.5852	1198	7	−1.0	1465	11	−1.6
0.6162	1204	12	−1.7	1470	12	−1.8
0.7044	1207	11	−1.5	1479	11	−1.6
0.7722	1208	8	−1.0	1486	9	−1.2
0.8691	1214	7	−0.8	1501	8	−1.0
1	1219	0	0	1520	0	0
			Cyclohexane (1)–*n*-Dodecane (2)			
		T = 298.15 K			T = 318.15 K	
0	987	0	0	1127	0	0
0.1132	995	9	−0.2	1142	4	−0.9
0.2224	1006	5	−1.0	1154	4	−0.9
0.3175	1017	9	−1.7			
0.3357				1169	6	−1.1
0.4122	1023	6	−1.1	1183	8	−1.5
0.4875	1035	11	−1.8	1196	9	−1.6
0.5638	1045	11	−1.8	1209	8	−1.3
0.6757	1059	10	−1.5	1230	5	−0.8
0.7909	1076	8	−1.0	1262	8	−1.1
0.8853	1093	5	−0.6	1290	6	−0.7
1	1120	0	0	1331	0	0
		T = 308.15 K			T = 333.15 K	
0	1052	0	0	1251	0	0
0.1132	1063	2	−0.5	1269	4	−1.0
0.2224	1073	3	−0.5	1286	5	−1.0
0.3175				1305	7	−1.5
0.3357	1088	6	−1.1			
0.4122	1098	7	−1.3	1325	10	−1.9
0.4875	1107	6	−1.1	1341	10	−1.8
0.5638	1119	7	−1.2	1358	9	−1.5
0.6757	1141	9	−1.4	1390	9	−1.4
0.7909	1165	10	−1.3	1426	6	−0.9
0.8853	1185	5	−0.6	1463	4	−0.5
1	1219	0	0	1520	0	0
			Cyclohexane (1)–*n*-Tetradecane (2)			
		T = 298.15 K			T = 318.15 K	
0	913	0	0	1039	0	0
0.1193	925	2	−0.7	1056	3	−0.8
0.1584	932	5	−1.2	1064	5	−1.2
0.2269	939	5	−1.2	1073	4	−0.9
0.2832	946	6	−1.3	1083	5	−1.1
0.3484	953	5	−0.7	1098	8	−1.8
0.4345	966	6	−1.2	1118	11	−2.2
0.4912	979	10	−1.8	1129	10	−1.9
0.5761	992	8	−1.5	1148	7	−1.3
0.6761	1015	10	−1.6	1178	7	−1.2
0.7570	1034	8	−1.2	1206	6	−0.9
0.8681	1064	3	−0.4	1252	3	−0.4
1	1120	0	0	1331	0	0

Table II (*Continued*)

x_1	κ_T/ TPa^{-1}	κ_T^E/ TPa^{-1}	$10^{-3}(\partial V^E/\partial p)_T$/ ($cm^3\ mol^{-1}\ TPa^{-1}$)	κ_T/ TPa^{-1}	κ_T^E/ TPa^{-1}	$10^{-3}(\partial V^E/\partial p)_T$/ ($cm^3\ mol^{-1}\ TPa^{-1}$)
		$T = 308.15$ K			$T = 333.15$ K	
0	973	0	0	1146	0	0
0.1193	987	2	−0.7	1167	2	−0.7
0.1584	995	5	−1.2	1178	5	−1.3
0.2269	1000	2	−0.4	1190	5	−1.2
0.2832	1009	3	−0.7	1203	6	−1.3
0.3484	1021	6	−1.2	1218	6	−1.3
0.4345	1040	10	−2.0	1241	7	−1.4
0.4912	1048	8	−1.5	1260	10	−1.9
0.5761	1064	6	−1.0	1285	7	−1.3
0.6761	1091	8	−1.3	1324	8	−1.3
0.7570	1116	9	−1.3	1359	6	−0.9
0.8681	1156	6	−0.8	1421	5	−0.6
1	1219	0	0	1520	0	0

Table III. Coefficients and Standard Deviation $\sigma(\kappa_T)$ for the Adjustment of κ_T According to Eq 3

T/K	A_0	A_1	A_2	A_3	$\sigma(\kappa_T$/ $TPa^{-1})$
		Cyclohexane (1)-*n*-Decane (2)			
298.15	1095.0	42.8	−18.1		0.9
308.15	1177.1	42.0			1.9
318.15	1265.7	49.6	14.3		1.8
333.15	1411.6	76.2	30.7		1.7
		Cyclohexane (1)-*n*-Dodecane (2)			
298.15	987.5	61.8	68.4		2.1
308.15	1053.5	60.8	102.9		1.9
318.15	1126.5	131.7	−42.1	114.7	1.2
333.15	1249.8	178.7	−67.6	157.9	1.4
		Cyclohexane (1)-*n*-Tetradecane (2)			
298.15	912.2	124.8	−57.8	139.5	1.7
308.15	972.1	138.2	−51.7	159.7	1.9
318.15	1037.2	184.0	−116.1	224.4	2.6
333.15	1144.4	218.6	−117.2	272.6	2.2

Table IV. Coefficients and Standard Deviation $\sigma(\kappa_T^E)$ for the Adjustment of κ_T^E According to Eq 7

T/K	B_0	B_1	$\sigma(\kappa_T^E$/ $TPa^{-1})$
	Cyclohexane (1)-*n*-Decane (2)		
298.15	47.1	17.8	1.0
308.15	43.2	16.3	2.0
318.15	38.8	0.1	1.5
333.15	46.5	25.7	1.6
	Cyclohexane (1)-*n*-Dodecane (2)		
298.15	36.6	20.8	1.4
308.15	32.4	24.2	1.1
318.15	36.1	11.3	1.6
333.15	38.1	1.7	0.7
	Cyclohexane (1)-*n*-Tetradecane (2)		
298.15	33.2	8.3	1.4
308.15	33.0	19.7	1.7
318.15	32.5	2.2	1.4
333.15	32.2	7.4	0.9

values are reported in Table II.

Very frequently published papers use the "excess" function defined by Orwoll and Flory (*10*) as

$$\kappa_T^E = -V^{-1}(\partial V^E/\partial p)_T = \kappa_T - \phi_1\kappa_{1T} - \phi_2\kappa_{2T} \quad (5)$$

where ϕ_i is the volume fraction of component i, that is

$$\phi_i = x_iV_i/V \quad (6)$$

where V is the mixture volume as calculated from eq 2. The "excess" isothermal compressibility κ_T^E is widely used by researchers (*10*, *11*) in the field, a reason that we have calculated it here. The κ_T^E values given in Table II for the four temperatures and three systems were fit to a polynomial of the type

$$\kappa_T^E = x_1x_2\{B_0 + (2x_1 - 1)B_1\} \quad (7)$$

The B_i coefficients and the standard deviations σ are given in Table IV.

The values of κ_T^E obtained through eq 7 were plotted against the cyclohexane mole fraction x_1. The three systems gave almost identical plots, similar in appearance, feature, and size. Figure 4 for the cyclohexane–*n*-tetradecane system is given as representative. The "excess" isothermal compressibility κ_T^E is positive for the three systems and has a maximum around $x_1 = 0.5$ for all temperatures. It is worth mentioning that the κ_T^E maximum is always less than 1% of the mixture compressibility. Therefore actual variation of κ_T^E with temperature cannot be deduced safely in any system as the observed variations are within experimental error.

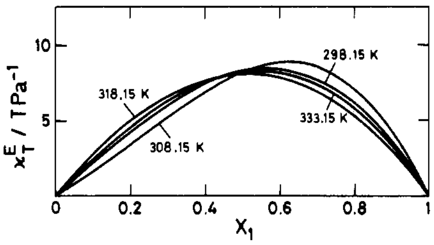

Figure 4. Plot of "excess" isothermal compressibility κ_T^E vs. cyclohexane mole fraction x_1 for the cyclohexane–*n*-tetradecane system.

Glossary

A_1, A_2, ..., A_i	coefficients in representation of isothermal compressibility by eq 3
B_0, B_1	coefficients in representation of "excess" isothermal compressibility by eq 7
p	pressure, Pa
T	temperature, K
V	molar volume, $cm^3\ mol^{-1}$
V^E	molar excess volume, $cm^3\ mol^{-1}$
x_i	mole fraction of component i

Greek Letters

ϕ_i	volume fraction of component i
κ_T	isothermal compressibility, TPa^{-1}
κ_T^E	"excess" isothermal compressibility, TPa^{-1}
ρ	density, g cm^{-3}
σ	standard deviation

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Vapor–Liquid Equilibrium for the *p*-Dioxane–Acetonitrile System at 298.15 K

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Isothermal vapor–liquid equilibrium data were determined by using a Boublik–Benson still for the *p*-dioxane–acetonitrile system at 298.15 K. The results obtained were correlated in terms of the liquid activity coefficients of the two components by two-suffix Margules and van Laar equations.

Vapor–liquid data are necessary for interpretation of distillation processes. This paper reports the results of measurements on vapor–liquid equilibrium for the *p*-dioxane–acetonitrile system at 298.15 K. Experimental data for this system have not been reported in the literature, and this system was chosen because *p*-dioxane (component 1) is nonpolar and acetonitrile (component 2) is polar.

Experimental Section

Acetonitrile (Carlo Erba p.a.) was distilled over dried P_2O_5 at reduced pressure, and only the middle half of each distillation was recovered. *p*-Dioxane (Baker p.a.) was distilled over sodium at reduced pressure, and again only the middle half of each distillation was recovered.

Densities were determined with a Robertson specific gravity bottle. The refractive indexes for the sodium D line of the pure components were measured with a Jena dipping refractometer with an accuracy of ±0.00002.

Equilibrium data were determined by using a modified version of the equilibrium still described by Boublik and Benson (*1*). The still and a water ebulloscope were attached to a large pressure vessel which could be maintained at any required pressure. The equilibrium value of the pressure was calculated from the boiling point of water in the ebulloscope. The latter could be determined with an accuracy of 0.01 °C by using a calibrated thermometer. The temperature in the still was also measured at 0.01 °C. Barometric pressure and room temperature were recorded for each experimental run, and necessary corrections were made on the observed pressure values. Compositions of the equilibrium liquid and condensed vapor phases were obtained from measurements of their refractive indexes at 298.15 K by using eq 1 (*2*), where x_1 is the molar fraction of *p*-dioxane.

$$n_D(x_1) = 0.93925x_1 + 0.76097(1 - x_1) + x_1(1 - x_1) \times [-0.21520 - 0.28471(2x_1 - 1) - 0.43586(2x_1 - 1)^2] \quad (1)$$

This equation correlates the results of a series of known composition mixtures of the two components. Table I gives densities, refractive indexes, and vapor pressures of the pure components and literature values for comparison.

Table I. Physical Properties of Pure Components at 298.15 K

	ρ		n_D		P^0	
compd	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.
p-dioxane	1027.1	1026.87	1.42021	1.42025	4.83	4.97[4]
acetonitrile	776.8	776.83	1.34135	1.34163	11.87	11.87[7]

[a] Reference 7.

Table II. Experimental and Calculated Isothermal Vapor–Liquid Equilibrium Results for *p*-Dioxane (1) plus Acetonitrile (2)

x_1	y_1	P	γ_1	γ_2
0.1125	0.0640	11.33	1.334	1.007
0.2000	0.1125	10.90	1.269	1.019
0.3070	0.1715	10.30	1.191	1.037
0.4005	0.2272	9.81	1.152	1.065
0.5170	0.3002	9.14	1.099	1.116
0.5506	0.3235	8.91	1.084	1.130
0.6470	0.4013	8.27	1.062	1.182
0.7465	0.4971	7.52	1.037	1.257
0.8130	0.5812	6.94	1.027	1.310
0.8988	0.7262	6.05	1.012	1.379
0.9300	0.7965	5.69	1.009	1.394

Results

The liquid-phase activity coefficients were estimated from the experimental data, taking into consideration the nonideality of the vapor phase by employing the following equation:

$$\ln \gamma_i = \ln \frac{y_i P}{x_1 P_i^0} + \frac{(B_{ii} - v_i^0)(P - P_i^0)}{RT} + (1 - y_i)^2 \frac{P\delta}{RT} \quad (2)$$

where

$$\delta = 2B_{12} - B_{11} - B_{22}$$

For *p*-dioxane at 298.15 K, $B_{11} = -1.948 \times 10^{-3}$ m^3 mol^{-1}; for acetonitrile at 298.15 K, $B_{22} = -3.722 \times 10^{-3}$ m^3 mol^{-1} and $B_{12} = -1.499 \times 10^{-3}$ m^3 mol^{-1}. These values were estimated from an empirical correlation (*6*).

Values of the molar fraction of *p*-dioxane in the liquid and vapor phases, the pressures, and the activity coefficients of both components are summarized in Table II.

Figure 1 shows the logarithm of the activity coefficients of both components vs. the molar fraction of *p*-dioxane.

A conventional thermodynamic consistency test was applied to the present system. It is a well-known area test that thermodynamically consistent isothermal test binary data should satisfy eq 3. However, some experimental error is inevitably

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} \, dx_1 = 0 \quad (3)$$

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