For mixtures, the constants *a* and *b* are given by the mixing rules

$$a = \sum_i \sum_j (1 - \delta_{ij}) x_i x_j a_i^{1/2} a_j^{1/2} \tag{5}$$

$$b = \sum_i x_i b_i \tag{6}$$

where δ_{ij} is a binary interaction parameter characteristic of the binary system $i + j$.

Binary interaction parameters were determined by a fit of the critical locus for each binary system. The objective function used may be expressed as

$$S = \sum_1 \left\{ \left| 1 - \frac{P_{c,n}^{\text{calcd}}}{P_{c,n}^{\text{exptl}}} \right| + \left| 1 - \frac{T_{c,n}^{\text{calcd}}}{T_{c,n}^{\text{exptl}}} \right| \right\} \tag{7}$$

The fit of the data is shown in terms of excess critical properties (actual critical property minus mole faction average property) in Figures 4 and 5. The optimum values of the parameters are given in the figures. The values are close to zero as would be expected for these simple nonpolar mixtures. The equation of state was then used to predict the phase envelopes of the binary systems (using the binary interaction parameters obtained from a fit of the critical locus). Typical calculated phase envelopes are shown in Figures 2 and 3. In general, the predictions were satisfactory. However, the predicted phase envelopes were, as a rule, too narrow. Deviations from the experimental data increased as the size differences between the components increased. We may therefore conclude that binary interaction parameters calculated from the critical locus should not be used to predict phase equilibria away from the critical region. This is a limitation of simple equations of state, since we did not reach this conclusion when a complex equation of state was used (*7*).

Glossary

a, b	constants in the Peng-Robinson equation
k	constant in the Peng-Robinson equation
P	pressure, MPa
R	gas constant
T	temperature, K
x	mole fraction
δ	binary interaction parameter
ω	acentric factor

Subscripts

1, 2	component 1, 2
c	critical
i, j	component i, j
n	nth data point

Superscripts

calcd	calculated
exptl	experimental

Registry No. 2-Methylpentane, 107-83-5; 2-methylhexane, 591-76-4; 2-methylheptane, 592-27-8; 2-methyloctane, 3221-61-2.

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Received for review September 21, 1987. Accepted February 26, 1988.

Isothermal Liquid–Vapor Equilibria of Mixtures Containing Organic Compounds. 2. Excess Gibbs Free Energies of a Hydrocarbon or Tetrachloromethane + a Cyclic Ketone at 298.15 K[†]

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Vapor–liquid equilibrium data for mixtures of heptane, cyclohexane, tetrachloromethane, or benzene with cyclopentanone or with cyclohexanone were determined at 298.15 K by headspace gas chromatographic analysis of the equilibrated vapor phase. Excess molar Gibbs free energies G^E for the examined mixtures were obtained by a least-squares treatment of the equilibrium results. G^E are positive for all systems except for benzene + cyclohexanone and, for each given cosolvent, are in the order cyclopentanone > cyclohexanone and heptane > cyclohexane > tetrachloromethane > benzene. Activity coefficients at infinite dilution as well as free energies of solvation were evaluated for all the solutes in all the solvents investigated here.

Introduction

As a continuation of our study on solute–solute–solvent interactions (*1*–*3*) both in water and nonaqueous solvents, here we report excess molar Gibbs energies G^E at 298.15 K of an apolar component (heptane, cyclohexane, tetrachloromethane, and benzene) + a cyclic ketone (cyclopentanone and cyclohexanone). These results will be used in forthcoming papers either to get the so-called Kirkwood–Buff integrals (*1*) or to test the applicability of a quasi-chemical group contribution model (*4*) to mixtures involving cyclic molecules.

A headspace gas chromatographic technique already used in experiments (*3*), which was proved simpler and faster than conventional static or dynamic methods, was employed for measuring vapor composition, y, as a function of liquid composition, x, over the whole composition range. G^E were obtained from the equilibrium results by a modification of Barker's method (*5*).

[†] Part I, ref *3*.

Apparatus and Method

The apparatus and procedure were described in detail in a previous work (*3*), where the reliability and suitability of headspace GC for obtaining x-y data was checked. Briefly, an equilibration cell was combined with a gas chromatograph for the analysis of the gas phase, air + vapors, at atmospheric pressure. The chromatographic column was a 2 mm × 2 m stainless-steel tube packed with methylsilicon polymer (SE30) on Chromosorb W 60-80. Only for the system benzene-cyclopentanone, Carbowax 20M was used. A hot-wire detector was employed in all experiments. Peak areas were obtained by means of a C. Erba Mega 2 integrator interfaced to the chromatograph. For a given liquid composition, the reproducibility of the area ratio A_1/A_2 of the two components was usually about 1%.

All mixtures were prepared by weighing. The uncertainty in the liquid mole fraction x, after correction for buoyancy and for evaporation of constituents, was estimated less than 0.04%, though becoming 10 times larger at extreme dilutions.

The values of y were obtained from the measured A_1/A_2 ratio and the response factor r_f of the chromatograph for the mixture under examination, by the equation

$$y = 1/[1 + r_f/(A_1/A_2)] \qquad (1)$$

The values of r_f for each pair of components were determined, by calibration analyses, through the equation

$$r_f = (A_1^*/A_2^*)/(p_1^*/p_2^*) \qquad (2)$$

where p_i^* is the vapor pressure of the ith pure component and (A_1^*/A_2^*) is the area ratio of the peaks obtained by separately injecting into the chromatograph equal volumes of the two vapors equilibrated with the pure liquids at 298.15 K. The overall uncertainty in y, resulting mostly from the uncertainty in A_1/A_2, was generally less than 1%.

Materials

Heptane, cyclohexane, cyclopentanone, and cyclohexanone were products from Fluka; benzene and tetrachloromethane from Carlo Erba. All chemicals were used without further purification. Purities, as checked by means of GC, were >99.5 mass %. Purity of substances is not a critical factor in consequence of the GC technique employed in determining the composition of vapors.

Data Treatment

For each liquid mixture of mole fraction x_i, the experimental ratio of the activity coefficients f_i of the constituents is given by

$$(f_1/f_2)_{\mathrm{exptl}} = (x_2/x_1)(p_2^*/p_1^*)(w_2/w_1)(A_1/A_2)(1/r_f) \qquad (3)$$

where the factor w_i, relevant to vapor-phase nonideality, was calculated taking into account also the presence of air in the vapor phase (*3*). In Table I are collected the values of the vapor pressure p^* and the molar volume V^* of the pure liquids, as well as values of the second virial coefficient B_{ii} of the pure gas i, and of the mixed virial coefficient B_{ij}, used in evaluating w_i, whose expression is given elsewhere (*3*, *9*).

The experimental values of the ratio f_1/f_2 in eq 3 were used in a nonlinear least-squares procedure, similar to that described by Barker (*5*) for the treatment of x-total pressure data. For this purpose, the sum S of the squared residuals extended over all n experimental points

$$S = \sum_{k=1}^{n} \{\ln (f_1/f_2)_{\mathrm{exptl}} - \ln (f_1/f_2)_{\mathrm{calcd}}\}_k^2 \qquad (4)$$

is minimized, and thus the coefficients c_i of the Redlich-Kister equation (*10*) (i, j = 1, 2; $i \neq j$)

$$\ln f_i = \{c_1 + 3(-1)^j c_2 + 5c_3\}x_j^2 - 4(-1)^j\{c_2 + 4(-1)^j c_3\}x_j^3 + 12c_3x_j^4 \qquad (5)$$

representing the activity coefficients f_i, appearing in the expression for $(f_1/f_2)_{\mathrm{calcd}}$, were determined. Also the response factor r_f of the gas chromatograph, appearing in the expression for $(f_1/f_2)_{\mathrm{exptl}}$ (eq 3), was treated as an adjustable parameter to be determined in the least-squares procedure.

Table I. Pure-Component Properties at 298.15 K Used in the Data Reduction

compd	p^{*a}/kPa	V_m^{*b}/(cm^3 mol^{-1})	$-B_{ii}{}^c$/(dm^3 mol^{-1})	$-B_{ij}{}^d$/(dm^3 mol^{-1})	
heptane	6.09	147.47	2.8	1.7	2.0
cyclohexane	13.01	108.75	1.7	1.3	1.56
benzene	12.68	89.41	1.48	1.2	1.45
tetrachloromethane	15.25	97.09	1.6	1.2	1.5
cyclopentanone	1.52	89.1^e	2.7^e		
cyclohexanone	0.62^f	104.18	3.3^e		
nitrogen			0.0	0.1^g	

[a] Vapor pressures from ref *6*. [b] Molar volumes from ref *7*. [c] Virial coefficients of pure components extrapolated from higher temperature data in ref *8*. [d] Cross virial coefficients computed according to ref *9*; for each compound, the first value refers to mixtures with cyclopentanone, the second one to mixtures with cyclohexanone. Most B_{ij} (and some B_{ii}) are affected by large uncertainties; however, the calculated w_i terms were found different from 1 by less than 2.5% for all mixtures, and partially compensating in the ratio w_2/w_1 (eq 3). [e] Estimated value. [f] Reference *7*. [g] Reference *8*; the same value applies for all mixtures of nitrogen (or oxygen) with the listed substances.

Minimizing the residuals of ln (f_1/f_2) was found the same as minimizing the relative residuals of A_1/A_2. This treatment of x - ln (f_1/f_2) was preferred to that of x-y, adopted previously (*3*), since it results in a better fitting of the activity coefficients of both components in the dilute regions.

Excess molar Gibbs energies G^E were computed from the parameters c_i in eq 5 through the equation

$$G^E/RT = x_1x_2[c_1 + c_2(x_1 - x_2) + c_3(x_1 - x_2)^2] \qquad (6)$$

By the calculation procedure described above, the activity coefficients of both components were obtained simultaneously in an analytical form (eq 5). A different method was also applied so as to calculate the activity coefficients f_1 and f_2 separately. The following equation, holding under the assumption of ideal behavior of vapor phase, was employed:

$$f_i = A_i/A_i^*x_i \qquad (7)$$

The area A_i, corresponding to the vapor in equilibrium with the mixture of mole fraction x_i, is divided by A_i^*, the area of the peak of the vapor equilibrated with its pure liquid. For all mixtures considered here, the f_i values obtained by this direct method were found to be reproduced within experimental error by the function (eq 5) derived from the least-squares treatment explained above. This is illustrated, as an example, in Figure 1 where the activity coefficient of both components is plotted against x for the system heptane-cyclopentanone.

Though either of the methods gives results comparable and equally reliable, we preferred the mathematical procedure which furnishes smoothed and thermodynamically consistent activity coefficients.

Results and Discussion

The experimental x-y quantities are reported in Table II. Table III gives the c_i values of eq 5 as well as the experimental and calculated values of r_f. On the average, the standard

Table II. Experimental Vapor–Liquid Equilibrium Data for Binary Systems at 298.15 K[a]

x	y	x	y	x	y
		$(x)n\text{-}C_7H_{16} + (1 - x)c\text{-}(CH_2)_4CO$			
0.0127	0.231	0.2902	0.748	0.8457	0.889
0.0235	0.314	0.3874	0.768	0.8936	0.908
0.0556	0.512	0.4302	0.779	0.9395	0.937
0.0795	0.563	0.5029	0.796	0.9739	0.9699
0.1455	0.676	0.5866	0.821	0.99064	0.9883
0.2177	0.720	0.7148	0.847		
		$(x)n\text{-}C_7H_{16} + (1 - x)c\text{-}(CH_2)_5CO$			
0.00312	0.118	0.2618	0.860	0.8098	0.952
0.01047	0.300	0.3588	0.885	0.8587	0.957
0.0241	0.492	0.4694	0.902	0.9161	0.9718
0.0540	0.665	0.5526	0.911	0.9387	0.9776
0.1072	0.787	0.6192	0.924	0.9732	0.9882
0.1829	0.840	0.6998	0.935	0.99439	0.9978
		$(x)c\text{-}C_6H_{12} + (1 - x)c\text{-}(CH_2)_4CO$			
0.00896	0.226	0.3963	0.890	0.9008	0.9588
0.0190	0.379	0.4867	0.906	0.9435	0.9718
0.0542	0.610	0.5740	0.911	0.9840	0.9896
0.0965	0.716	0.6732	0.923	0.99137	0.9939
0.1810	0.808	0.7691	0.936		
0.2936	0.862	0.8373	0.947		
		$(x)c\text{-}C_6H_{12} + (1 - x)c\text{-}(CH_2)_5CO$			
0.00591	0.262	0.3039	0.937	0.7989	0.976
0.01065	0.372	0.4021	0.950	0.8999	0.9858
0.0257	0.602	0.5184	0.958	0.9586	0.9927
0.0747	0.805	0.5997	0.967	0.9824	0.9965
0.1255	0.866	0.6913	0.971		
0.2082	0.914	0.7974	0.978		
		$(x)C_6H_6 + (1 - x)c\text{-}(CH_2)_4CO$			
0.01957	0.153	0.3994	0.851	0.8996	0.9849
0.06259	0.371	0.4993	0.890	0.9495	0.9930
0.1451	0.587	0.6143	0.934	0.9652	0.9951
0.2200	0.710	0.6857	0.948	0.9754	0.9965
0.3119	0.789	0.8133	0.973	0.9764	0.9971
		$(x)C_6H_6 + (1 - x)c\text{-}(CH_2)_5CO$			
0.00909	0.158	0.2582	0.868	0.8109	0.9900
0.02870	0.365	0.3719	0.920	0.8981	0.9948
0.0615	0.560	0.4621	0.944	0.9731	0.9988
0.1101	0.703	0.5510	0.961	0.9867	0.9994
0.1799	0.800	0.6713	0.979		
		$(x)CCl_4 + (1 - x)c\text{-}(CH_2)_4CO$			
0.01834	0.195	0.2651	0.805	0.7373	0.9619
0.0352	0.302	0.3797	0.875	0.8472	0.9774
0.0845	0.529	0.4908	0.908	0.9464	0.9920
0.1568	0.703	0.6180	0.938	0.9896	0.9985
		$(x)CCl_4 + (1 - x)c\text{-}(CH_2)_5CO$			
0.00721	0.172	0.2902	0.914	0.7959	0.9893
0.0283	0.431	0.4116	0.944	0.8747	0.9937
0.0534	0.587	0.4996	0.9613	0.9725	0.9987
0.1106	0.750	0.5922	0.9724		
0.1967	0.862	0.6877	0.9829		

[a] y values were obtained from eq 1 by using the least-squares r_f's from Table III.

deviation s for the representation of ln (f_1/f_2) amounts to 0.04; the one for y, not reported in Table III, was found to be 0.005. For most systems examined here, an equally good reproduction of the experimental behavior is obtained if the Wilson equation (*10*), instead of the Redlich–Kister one (eq 5), is used.

In Figure 2 the plots of y and ln (f_1/f_2) vs x are shown for the system cyclohexane–cyclohexanone. The data of Boublik and Lu (*11*) at 323.15 K are also reported for comparison. We do not know of any other result in the literature which can be used for comparison with any one of our mixtures.

In Figure 3 is illustrated the behavior of G^E for all systems examined. With the exception of the tetrachloromethane–cyclopentanone system, all mixtures exhibit positive deviations, which, for a given ketone, decrease in the order heptane, cy-

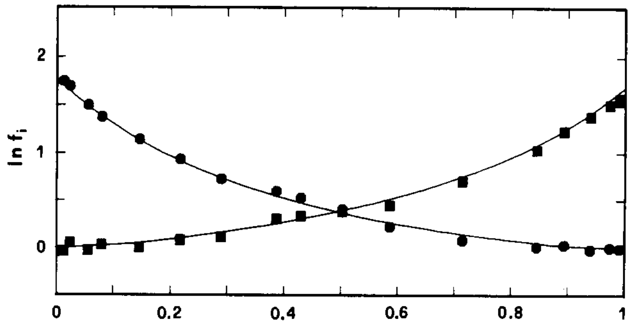

Figure 1. Plot of ln f_1 and ln f_2 against x_1 for the heptane (1)–cyclopentanone (2) system at 298.15 K: (●) experimental ln f_1 (eq 7); (■) experimental ln f_2 (eq 7); (—) calculated from eq 5 with parameters from Table III.

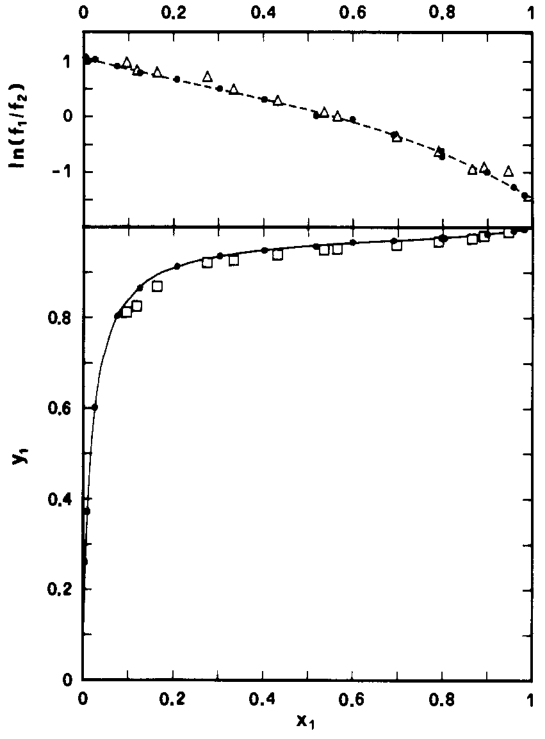

Figure 2. Plot of y_1 (lower curve) and ln (f_1/f_2) (upper curve) against x_1 for the system cyclohexane (1)–cyclohexanone (2): (●) present work (298.15 K); (□) ref 11 (323.15 K); (△) evaluated by us from x-y-P at 323.15 K from ref 11; (– – –) calculated from eq 5 with parameters from Table III; (—) calculated as $y_1 = 1/[1 + (p_2^*/p_1^*)(f_2/f_1)(w_2/w_1)]$ with f_i from eq 5.

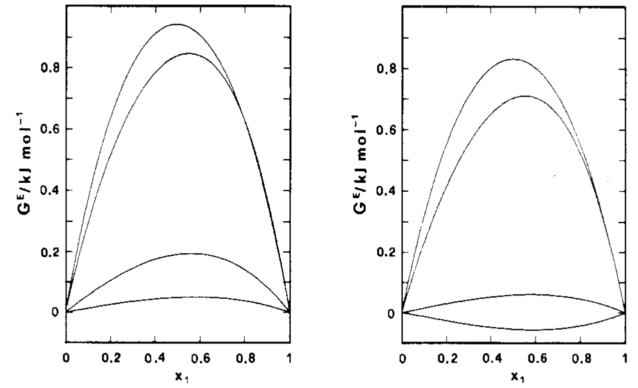

Figure 3. Comparison between calculated G^E curves for A (1)–cyclopentanone (2) systems (on the left), and those for A (1)-cyclohexanone (2) (on the right). From top to bottom: A = heptane, cyclohexane, tetrachloromethane, benzene.

Table III. Least-Squares c_i Coefficients of Eq 5, Chromatographic Response Factor r_f, Standard Deviation s for Representation of ln (f_1/f_2), and Gibbs Excess Free Energy G^E at $x = 0.5$ for Binary Systems at 298.15 K

system							
compd 1	compd 2	c_1	c_2	c_3	r_f[a]	s	$G^E(x=0.5)$[b]/ (J mol^{-1})
n-C_7H_{16}	c-$(CH_2)_4CO$	1.5165	−0.0397	0.1984	1.050 (1.02)	0.039	940
n-C_7H_{16}	c-$(CH_2)_5CO$	1.3381	−0.0140	0.1315	0.893 (0.92)	0.050	829
c-C_6H_{12}	c-$(CH_2)_4CO$	1.3537	0.2216	0.2274	0.807 (0.78)	0.035	839
c-C_6H_{12}	c-$(CH_2)_5CO$	1.1319	0.2165	0.1231	0.680 (0.65)	0.038	701
C_6H_6	c-$(CH_2)_4CO$	0.0794	0.0269		0.806 (0.84)	0.047	49
C_6H_6	c-$(CH_2)_5CO$	−0.0877	−0.0331		0.625 (0.61)	0.048	−54
CCl_4	c-$(CH_2)_4CO$	0.3087	0.0734		0.971 (0.94)	0.037	191
CCl_4	c-$(CH_2)_5CO$	0.0937	0.0320		0.766 (0.74)	0.052	58

[a] Chromatographic response factor determined by least-squares method; values in parentheses are the experimental r_f's (eq 2). [b] An average uncertainty on G^E at $x = 0.5$ of 10 J mol^{-1} was calculated from the error on c_i coefficients.

Table IV. Activity Coefficients at Infinite Dilution f_i^∞ and Standard Molar Gibbs Free Energies of Solvation $\Delta G°_i$ of the Components of Binary Systems at 298.15 K

system	f_1^∞	$-\Delta G°_1$[a]/ (kJ mol^{-1})	f_2^∞	$-\Delta G°_2$[a]/ (kJ mol^{-1})
heptane (1)–cyclopentanone (2)	5.78	16.54	5.34	18.94
heptane (1)–cyclohexanone (2)	4.41	16.82	4.29	21.71
cyclohexane (1)–cyclopentanone (2)	3.89	15.64	6.07	19.37
cyclohexane (1)–cyclohexanone (2)	2.82	16.05	4.36	22.43
benzene (1)–cyclopentanone (2)	1.05	18.95	1.11	24.07
benzene (1)–cyclohexanone (2)	0.95	18.81	0.89	26.85
tetrachloromethane (1)–cyclopentanone (2)	1.27	18.02	1.47	23.17
tetrachloromethane (1)–cyclohexanone (2)	1.06	18.08	1.13	26.06

[a] $\Delta G°_i$ is referred to the process of eq 8 and evaluated as $\Delta G°_i = RT \ln (f_i^\infty p_i^* V_j^* / 8314.7T)$. The value for the standard process: component (ideal gas, 101.325 kPa) = component (solute obeying Henry's law, at unit mole fraction), can be calculated as $\Delta G°_i = RT \ln (f_i^\infty p_i^* / 101.325)$.

clohexane, benzene, tetrachloromethane. Furthermore, for a given apolar cosolvent, the G^E curves of mixtures with cyclopentanone are higher than those with cyclohexanone. The G^E curves are a little asymmetrical with their extremum at $0.55 < x < 0.6$, except for mixtures with n-hexane showing a maximum at $x \simeq 0.5$.

In Table IV are collected the values of the activity coefficient at infinite dilution, f_i^∞, obtained from the parameters of the fitting eq 5, as well as the standard molar Gibbs free energies of solvation $\Delta G°_i$ of the substances here considered. These $\Delta G°_i$ are referred to the transfer process

$$\text{component (ideal gas, 1 mol dm}^{-3}\text{)} = \text{component (solute obeying Henry's law, 1 mol dm}^{-3}\text{)} \quad (8)$$

By examination of the $\Delta G°_2$ values of ketones, an average increment of −2.9 kJ mol^{-1} is observed in going from cyclopentanone to cyclohexanone independently of component 1. This value, which represents the standard molar Gibbs energy change for the solvation in apolar solvents of a CH_2 group of cyclic molecules, is lower in magnitude than the value of −3.5 kJ mol^{-1} found for the solvation in tetrachloromethane of a CH_2 group of open-chain molecules (*3*).

Glossary

A_i	peak area of component i in the vapor phase
A_i^*	peak area of pure vapor of i
B_{ij}	second virial coefficient due to interaction of molecules i and j (i, j = 1, 2), dm^3 mol^{-1}
c_i	coefficients for eq 5
f_i	activity coefficient of component i
f_i^∞	activity coefficient of i at infinite dilution
G^E	excess Gibbs free energy, J mol^{-1}
$\Delta G°_i$	Gibbs free energy of solvation of i (eq 8), kJ mol^{-1}
n	number of experimental x,y couples
p_i^*	vapor pressure of pure liquid i, kPa
R	gas constant, J mol^{-1} K^{-1}
r_f	response factor of gas chromatograph
s	standard deviation of the fit
S	sum of residuals
T	absolute temperature, K
V_i^*	molar volume of pure liquid i, cm^3 mol^{-1}
w_i	vapor-phase non-ideality factor of i
x_i	liquid-phase mole fraction of i
y_i	vapor-phase mole fraction of i

Registry No. n-C_7H_{16}, 142-82-5; c-C_6H_{12}, 110-82-7; CCl_4, 56-23-5; C_6H_6, 71-43-2; c-$(CH_2)_4CO$, 120-92-3; c-$(CH_2)_5CO$, 108-94-1.

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Received for review January 8, 1987. Accepted February 11, 1988.