

Vapor—Liquid Equilibrium for Binary Mixtures of Isomeric *n*-Octenes with Some Solvents

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Measurements of isobaric temperature—liquid composition are reported in the binary systems formed from 1-octene, *cis*-4-octene and *trans*-4-octene with methyl cellosolve (2-methoxyethanol), 1-butanol and tetrachloroethene at pressures of 760 and 200 mm Hg (101.325 and 26.664 kPa). These systems have minimum boiling azeotropes. The *Wilson* equation is used to predict the liquid phase activity coefficients. The γ_i-x_i functions thus obtained are compared in the systems containing a solvent common to the three isomeric *n*-octenes.

(Keywords: *n*-Alkenes; Azeotropes; Phase equilibria)

Dampf-flüssig Gleichgewicht für binäre Mischungen von isomeren n-Octenen mit einigen Lösungsmitteln

Es werden thermodynamische Daten (isobare Siedetemperatur—Zusammensetzung der flüssigen Phase) und die Azeotrope der binären Systeme aus 1-Octen, *cis*-4-Octen und *trans*-4-Octen mit Methylcellosolv (2-Methoxyethanol), 1-Butanol und Tetrachlorethen bei Drücken von 760 mm Hg (101,325 kPa) und 200 mm Hg (26,664 kPa) angegeben. Die *Wilson*gleichung wurde zur Vorhersage der Aktivitätskoeffizienten in flüssiger Phase eingesetzt. Die so erhaltenen γ_i-x_i Funktionen werden für Mischungen der drei isomeren *n*-Octene mit jeweils einem gemeinsamen Lösungsmittel verglichen.

Introduction

The prediction of thermodynamic properties of pure components and their mixtures as well as vapor—liquid equilibrium data are essential for the process design and for the evaluation of many chemical and engineering operations. The thermodynamic properties and equilibrium data concerning mixtures of isomeric *n*-octenes with *n*-octane have recently been discussed^{1,2}. There are very few experimental results for the mixtures containing isomers of the *n*-alkene with other

solvents^{3,4}. Only vapor—liquid equilibrium data for the systems with 1-alkenes have been reported^{5–10}. The very similar properties of the isomers of *n*-alkenes, boiling temperatures first of all, appeared to permit a possibility of using in technical calculating the vapor—liquid equilibrium data on the systems with 1-alkenes for the systems consisting of their positional and configurational isomers. The purpose of our work was to test this supposition.

Table 1. *Purity and Antoine constants of components*

Component	%	Antoine constants		
		<i>A</i>	<i>B</i>	<i>C</i>
1. Methyl cellosolve	99.9	7.42251	1511.81	208.579
2. 1-Butanol	99.98	7.46281	1355.05	178.055
3. Tetrachloroethene	99.9	7.05050	1431.43	222.213
4. 1-Octene	99.96	6.95197	1362.52	213.356
5. <i>cis</i> -4-Octene	99.9	6.85944	1312.28	207.226
6. <i>trans</i> -4-Octene	99.98	6.89298	1326.62	208.234

Materials

Methyl cellosolve, 1-butanol and tetrachloroethene, laboratory reagent materials were fractionally distilled many times in a teflon bristle 50-plate column¹. Purities reported in Table 1 were detected by GLC on 50 m × 0.25 mm id squalane capillary column, using flame ionization detector. Additionally, *cis*-isomer of *n*-octene was checked in 3.7 m × 3 mm id AgNO₃ + 1,6-hexanediol column. Individual isomers of *n*-octene were synthesized from the corresponding *n*-alkynes by selective hydrogenation^{11,12}. The first purification was carried out as described above. Additional purification of 1) *cis*- and 2) *trans*-isomers was carried out by preparative gas chromatography on PGK-9 instrument (Estonian SSR) equipped with 3–5 m × 10–18 mm id stainless steel columns. The column packings were:

1) 29.6% 1,6-hexanediol and 9.7% AgNO₃ on 45–60 mesh Chromaton N-AW,

2) Apiezon L on 45–60 mesh Chromaton N-AW.

The temperatures used were 60 °C and 120 °C for the columns with AgNO₃ and Apiezon L, respectively. The carrier gas was nitrogen 12–18 dm³ h⁻¹.

Experimental Results and Correlation of Data

Boiling temperatures for the nine systems studied were measured as a function of liquid composition at total pressures of 760 and 200 mm Hg (101.325 and 26.664 kPa). The semi-micro ebulliometric method¹⁰ was used*. The measured boiling points were correlated using

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the *Wilson* equation. The *Wilson* parameters were obtained by a least-squares fit. The experimental results and the *Wilson* parameters derived without including vapor phase nonideality corrections are given in Table 2.

All binary systems investigated exhibit positive azeotropes whose compositions and boiling temperatures were determined by plotting α_{ik} and t against x_i , respectively. Table 3 shows the azeotropic parameters.

Table 3. *Azeotropic data at pressures*

Azeotrope	760 Torr		200 Torr	
	t , bp/°C	x_1	t , bp/°C	x_1
Methyl cellosolve (1) —				
— 1-octene (2)	107.6	0.470	69.3	0.410
— <i>cis</i> -4-octene (2)	108.1	0.490	70.0	0.420
— <i>trans</i> -4-octene (2)	107.9	0.490	69.6	0.430
1-Butanol (1) —				
— 1-octene (2)	108.7	0.489	71.9	0.365
— <i>cis</i> -4-octene (2)	109.2	0.530	72.7	0.380
— <i>trans</i> -4-octene (2)	109.0	0.531	72.5	0.380
Tetrachloroethene (1) —				
— 1-octene (2)	120.0	0.590	78.3	0.597
— <i>cis</i> -4-octene (2)	120.5	0.710	78.7	0.697
— <i>trans</i> -4-octene (2)	120.3	0.670	78.5	0.680

The experimentally determined boiling points of compounds were correlated by means of the *Antoine* equation

$$\log P_i^\circ = A - \frac{B}{C + t(^{\circ}\text{C})}$$

The components were repeatedly checked for purity by measuring the boiling points and by using capillary gas chromatography. The duplicate measurements agreed with previous measurements (see Table 1) within experimental error¹⁰.

Discussion

The activity coefficients of components calculated from the *Wilson* equation for systems containing methyl cellosolve, 1-butanol and tetrachloroethene are plotted in Fig. 1 (*a*, *b*, *c*, respectively) as functions of liquid composition at normal pressure. Fig. 1 clearly indicates that

all compounds studied exhibit a positive deviation from *Raoult's* law. The activity coefficients decrease numerically as the polarity of the solvent decreases from methyl cellosolve to tetrachloroethene. The last one has a zero dipole moment. As is shown in Fig. 1 *a* and *1b*, there is a very close interaction between each couple of components in the systems containing a polar common solvent. The relative greater differences in the values of activity coefficients in the systems with

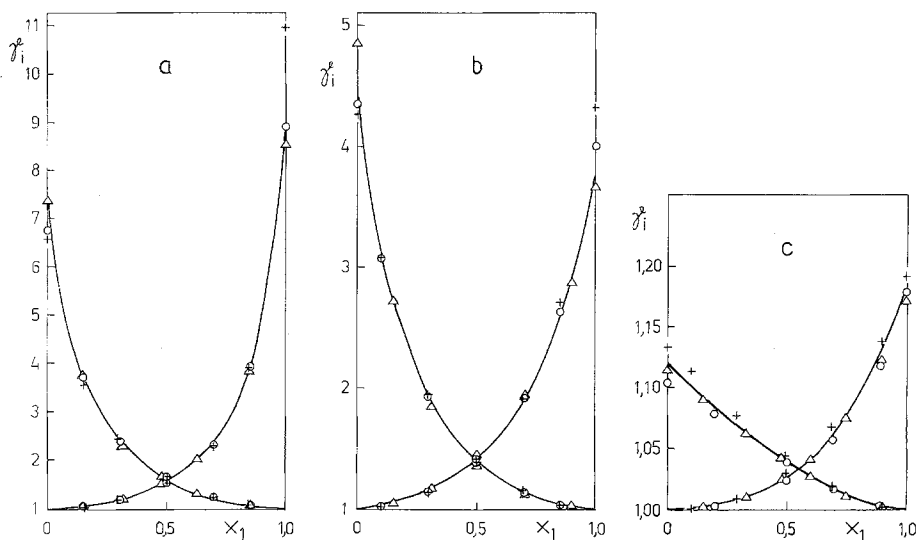


Fig. 1. Activity coefficients for systems. *a* Methyl cellosolve (1)—*n*-octene (2) \circ = *cis*-4-octene, *b* 1-Butanol (1)—*n*-octene (2) $+$ = *trans*-4-octene, *c* Tetrachloroethene (1)—*n*-octene (2) Δ = 1-octene

tetrachloroethene are probably due to an interaction between the π -electrons of the double bonds.

From the results shown above it is clear that by using the activity coefficients of the well studied mixtures with 1-alkenes the vapor-liquid equilibrium can be predicted for the systems containing other isomers of the *n*-alkene as well. The prediction becomes more accurate if the common solvent is polar. The results obtained at pressure 200 Torr confirm also this conclusion.

Nomenclature: t = temperature, $^{\circ}\text{C}$; P_i° = vapour pressure of pure component i , torr; x_i = mole fraction of component i in the liquid phase; γ_i = liquid phase activity coefficient of component i ; A , B , C = constants of *Antoine* equation; Λ_{12} , Λ_{21} = parameters in the *Wilson* equation; α_{ik} = the relative volatility of binary system $i-k$.

References

- ¹ *Kuus, M., Kudryavtseva, L., Eisen, O.*, Eesti NSV Tead. Akad. Toim., Keem. **29**, 25 (1980).
- ² *Kuus, M., Toome, M., Kudryavtseva, L., Eisen, O.*, Eesti NSV Tead. Akad. Toim., Keem. **29**, 32 (1980).
- ³ *Woycicki, W.*, J. Chem. Thermodyn. **7**, 77 (1975).
- ⁴ *Woycicki, W.*, J. Chem. Thermodyn. **7**, 1007 (1975).
- ⁵ *Kudryavtseva, L., Viit, H., Eisen, O.*, Eesti NSV Tead. Akad. Toim., Keem. Geol. **18**, 346 (1969).
- ⁶ *Kudryavtseva, L., Viit, H., Eisen, O.*, Eesti NSV Tead. Akad. Toim., Keem. Geol. **19**, 22 (1970).
- ⁷ *Suryanarayana, Y. S., van Winkle, M.*, J. Chem. Eng. Data **11**, 7 (1966).
- ⁸ *Hanson, D. O., van Winkle, M.*, J. Chem. Eng. Data **12**, 319 (1967).
- ⁹ *Tassios, D., van Winkle, M.*, J. Chem. Eng. Data **12**, 555 (1967).
- ¹⁰ *Mihkelson, V., Kirss, H., Kudryavtseva, L., Eisen, O.*, Fluid Phase Equilibria, 201 (1977/1978).
- ¹¹ *Henne, A. L., Greenlee, K. W.*, J. Amer. Chem. Soc. **10**, 2020 (1943).
- ¹² *Brown, C. A., Ahuja, V. K.*, J. Org. Chem. **38**, 2226 (1973).