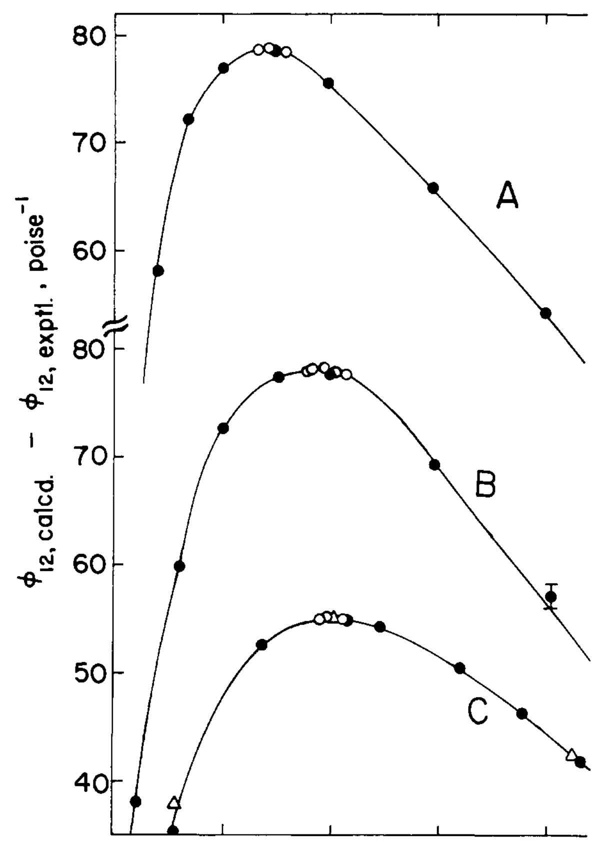

Figure 1. Difference between calculated and experimental fluidities of water-ether systems as a function of composition

○ Present work

A. Component 2, diethylene glycol dimethyl ether
● From (12)

B. Component 2, ethylene glycol dimethyl ether
● From (11)

C. Component 2, dioxane
● From (9)
△ From (4)

Table I. Composition and Fluidity of Aqueous Ether Solutions at the Point of Maximum Deviation in Fluidity

Component 2	x_2	x_1/x_2E[a]	$\phi_{12\,\text{exptl.}}$, Poise^{-1}	$\phi_{12\,\text{calcd.}}$,[b] Poise^{-1}	Dev.,[c] %
Dioxane	0.201	1.988	50.88[d]	105.90	108
Ethylene glycol dimethyl ether	0.193	2.091	50.47[e]	128.72	155
Diethylene glycol dimethyl ether	0.142	2.014	31.45[e]	110.27	251

[a] E is number of ether oxygens per molecule. [b] Calculated by Equation 1. [c] Deviation = 100 $(\phi_{12\,\text{calcd.}} - \phi_{12\,\text{exptl.}})/\phi_{12\,\text{exptl.}}$ [d] Based on viscosity of 0.008903 poise for water, to conform with (9). [e] Based on viscosity of 0.008940 poise for water, to conform with (11, 12).

ene oxide group for hexadecyl alcohol.7 EO to 5.7 for hexadecyl alcohol.21 EO (2, 3). The explanation of Elworthy and Macfarlane (3) that the increase in micellar hydration with higher ethylene oxide chain length is due to trapping of water within the mesh of polyoxyethylene chains is consistent with the present data on model ethers: Since two is the maximum number of water molecules that can be bound to each ether linkage by secondary valence forces, the excess water must be held by the micelle in a different manner.

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Ultraviolet and Infrared Spectra of Some Nitroindoles and Nitroindole-3-carboxaldehydes

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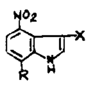
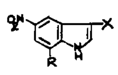
IN CONNECTION with recent synthetic studies in the indole field (3-7), a number of nitroindole-3-carboxaldehydes have been prepared (3,4,6,7) (Table II, 4a-7c) by the Vilsmeier reaction, involving formylation of the precursor nitroindoles (5) (1a-3c) prepared via the Fischer indole synthesis. In view of the usefulness of spectral data, particularly in the ultraviolet region, in structural studies (9) concerning the location of the nitro group in nitroindoles, the ultraviolet and infrared data which have been obtained are recorded (Tables I and II). The data in Table I supplement ultraviolet data recently summarized for nitro-3-acylindoles (9,10).



1, X = H
4, X = CHO



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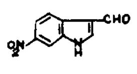
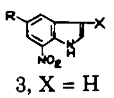


6



3, X = H
7, X = CHO

Nitroindoles, X = H:	Nitroindole-3-carboxaldehydes, X = CHO:
1a, 2a, 3a, R = H	4a, 5a, 7a, R = H
1b, 2b, 3b, R = CH_3	4b, 5b, 7b, R = CH_3
3c, R = OCH_3	7c, R = OCH_3
	and 6

The data in Table I show that replacement of a hydrogen (4a, 5a) by a methyl group (4b, 5b) in the 7-position of 4-

Ultraviolet and infrared spectral data are reported for a number of benzene ring–substituted nitroindoles and nitroindole-3-carboxaldehydes, and the effect of additional substituents, such as methyl or methoxyl, in the benzene ring is noted. A marked change occurs in the ultraviolet spectra of 4- and 5-nitroindole-3-carboxaldehyde upon replacement of the hydrogen in the 7-position by a larger methyl group. A similar change does not occur in the ultraviolet spectra of the corresponding nitroindoles.

Table I. Ultraviolet Spectra of Nitroindoles

Compound	Ref.	$\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ mμ(log ε)[a]			
1a	(*9*)[b]	236 (4.03)		282[c] (3.38)	380 (3.78)
1b(*5*)	. . .	238 (4.00)			379 (3.84)
2a	(*11*)[d]			265 (4.25)	324 (3.92)
2b(*5*)	. . .		253[c] (4.17)	268 (4.23)	329 (3.88)
3a	(*11*)[e]	232 (3.97)	250 (3.89)		365 (3.86)
3b(*5*)	. . .	233[c] (3.96)	252[c] (3.83)		378 (3.86)
3c(*5*)	. . .	230[c] (4.08)	250[c] (3.78)		400 (3.80)
4a(*4*)		266 (4.36)		287 (3.98)	355 (3.64)
4b(*7*)	. . .		257 (4.07)	290 (3.89)	361 (4.18)
5a(*4*)	[g]	236[c] (4.17)	257 (4.42)	262[c] (4.41)	313 (3.97)
5b(*7*)	. . .	235 (3.95)			366 (4.11)
6(*4*)	[h]			278 (4.56)	316[c] (4.07)
7a(*6*)	. . .	222 (4.28)		268 (4.15)	345 (4.03)
7b(*7*)	. . .	224 (4.28)		269 (4.11)	355 (3.97)
7c(*7*)	. . .	225 (4.31)	236[c] (4.15)	268 (4.12)	375 (3.84)

[a] Ultraviolet spectra determined in 1-cm. cells on a Cary Model 11 recording spectrophotometer. [b] Also reported (*11*) for la: 235 (4.04), 380 (3.81); and for 6-nitroindole (*11*): 250 (4.00) 326 (3.92), 355–360[c] (3.89), or (*1*); 250 (4.00), 326 (3.93), 354–360 (3.90). [c] Inflection. [d] Also reported (*1*): 266 (4.26), 325 (3.93). [e] Also reported (*12*): 232, 242–251 plateau with slight maximum at 248–250, 364. [f] Also reported (2): 227 (4.30), 287 (3.94), 357 (3.63). [g] Also reported (2): 258 (4.39), 313 (3.94), or (*12*): 257 (4.41), 263[c] (4.40), 312 (3.96). [h] Also reported (2): 278 (4.41), 310–320[c] (3.89). Other values reported (8) and subsequently quoted (9), 278 (4.23), 316[c] (3.72), are apparently low by 0.30 in log ε (equivalent to a factor of 2 in concentration).

Table II. Infrared Spectra

Compound[a]	Infrared Bands,[b] Cm.$^{-1}$ NH	C=O	C=C	NO_2
		Nitroindoles		
1b	3350ms	. . .	1620mw 1590m	1500ms, 1485ms 1310vs
2b	3340s	. . .	1615m 1595mw	1520m 1325vs, 1295vs
3b	3400s	1745mw[c]	1640mw 1580m 1525m	1500s 1360s[d] 1295vs
3c	3410m	. . .	1640mw 1580m 1530ms	1485s 1350ms[e] 1300vs
		Nitroindole-3-carboxaldehydes		
4a	3360mw	1650s	1620ms 1565m	1520s 1510s, 1500s 1315s, 1285s[f]
4b	3300m	1660s	1620m 1590mw	1525s 1340ms, 1290m
5a	3120ms	1650s	1625ms 1590ms	1535ms, 1520ms 1345s, 1330s 1295s
5b	3340w	1640s	1580s	~1500s[g] 1355s, 1315s
6	3200m	1645s	1620ms 1595ms	1515s, 1490ms 1340s
7a	3410mw 3100m	1665ms 1650s	1625ms 1580mw	1540s 1515ms, 1485ms 1365ms, 1330s 1285s
7b	3400m	1660s	1580m	1540s, 1525ms 1360ms, 1335m 1320ms, 1285s
7c	3350m	1680ms	1640mw 1585m	1540s, 1515s 1495s 1355s, 1320s 1290s

[a] References to the preparation of compounds are cited in Table I. [b] Infrared spectra determined in halocarbon oil and Nujol mulls on Unicam SP.200 spectrophotometer, and are reported to nearest 5 cm.$^{-1}$ below and nearest 10 cm.$^{-1}$ above 2000 cm.$^{-1}$. Relative intensities of bands, vs = very strong, s = strong, m = medium, w = weak. All major bands occurring in carbon-to-carbon double bond stretching and nitro regions of the spectra are reported. While splitting of bands is not unusual in solid phase spectra such as are reported here, some bands may be due to other functional groups, particularly in the nitro region of the spectra. This is especially likely in the symmetric stretching region of the nitro group (1290–1360 cm.$^{-1}$), where methyl bands also commonly occur. [c] Possibly an aromatic combination band of stronger than usual intensity; sample appeared to be homogeneous by thin layer chromatography with 1:1 ethyl acetate-benzene on E. Merck silica gel G. [d] Probably a methyl band. [e] Probably a methyl band of methoxyl group. [f] Also bands at 1365s and 1340s cm.$^{-1}$. [g] Inflection; partly obscured by Nujol band.

and 5-nitroindole-3-carboxaldehyde causes a marked change in at least one band in the ultraviolet spectrum. Thus, the band at 226 mμ in 4a is replaced by a band at 257 in 4b; the band at 257 and inflection at 262 in 5a disappear in 5b, while the band at 313 in 5a shifts to 366 mμ in 5b. In contrast, replacement of a hydrogen (7a) by a methyl group (7b), or even by a much more powerfully electron-releasing methoxyl group (7c), causes a less marked change in the ultraviolet spectrum of 7-nitroindole-3-carboxaldehyde, involving primarily a bathochromic shift in the long wavelength band, from 345 (7a) to 355 (7b) to 375 mμ (7c). These observations show that a change from hydrogen to methyl in the steric environment at the 7-position, ortho to the indole nitrogen—the primary source of electrons for conjugation—has a marked effect on the electron distribution within the molecules. In the corresponding nitroindoles (1a, 2a compared to 1b, 2b; and 3a compared to 3b and 3c), where the electron-withdrawing formyl substituent is absent, there is no similar effect.

ACKNOWLEDGMENT

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Relative Volatility of Hexane-C_6 Olefin Systems in *N,N*-Dimethylformamide

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Vapor-liquid equilibrium data at 400 and 760 mm. of mercury pressure were determined at preselected concentrations of *N,N*-dimethylformamid in ternary mixtures for the systems *n*-hexane–hexene-1, *n*-hexane–4-methyl-1-pentene, and *n*-hexene–2-methyl-1-pentene to determine solvent selectivity for the different olefins. Selectivity of the solvent for 2-methyl-1-pentene was slightly greater than that for the 4-methyl-1-pentene and somewhat greater than that for the hexene-1.

THE SEPARATION of compounds of similar volatility by the use of extractive distillation in which a solvent component is added to change the volatility of one or more of the components in the mixture relative to others, has become an important process in those industries utilizing distillation as a separations process. Selection of a solvent which will be effective in modifying the volatilities of the components of interest requires either extensive vapor-liquid equilibrium data on the mixture, including various solvents, or some means of predicting solvent effectiveness from a small amount of data. At present there is no satisfactory way to predict vapor-liquid equilibrium data from pure component properties, although equilibrium data for multicomponent systems can be predicted with some ternary data. This investigation is another of a series (*3, 5–9, 11,* and *12*) whose purpose is to determine experimentally the effect of various types of solvents on the relative volatility of components in mixtures. Specifically, this investigation was conducted to study the effect of the concentration of *N,N*-dimethylformamide on the paraffin-olefin systems of *n*-hexane–hexene-1, *n*-hexane–4-methyl-1-pentene, and *n*-hexane–2-methyl-1-pentene at two pressures, 400 and 760 mm. of Hg. The isomeric olefins were chosen so that the effects, if any, of branching and molecular size could be determined.

MATERIALS

n-Hexane and hexene-1 were obtained from the Phillips Petroleum Co. and 4-methyl-1-pentene (4M1P) and 2-methyl-1-pentene (2M1P) were obtained from K & K Laboratories. The solvent, *N,N*-dimethylformamide (DMF), was obtained from Matheson, Coleman, and Bell. Table I compares values of the physical properties of the materials determined experimentally and reported in the literature.

APPARATUS AND PROCEDURE

The vapor-liquid equilibrium data were determined using a modified Colburn still (*4*) described by Prabhu (*7*). Temperature was measured to within ±0.1° C. with a copper-constantan thermocouple, and the pressure was measured to within ±0.2 mm. of Hg. Complete analyses of the vapor and liquid samples were performed using a Beckmann GC2A Chromatograph equipped with a Sargent Recorder and a Disc Integrator. Since DMF and hexane are partially immiscible at room temperature, a third component, trichloropropane, was used to form single phase samples for introduction into the chromatograph. The analyses required two columns—one separating the hexane and the olefin, and the other separating the total hydrocarbons from DMF.

DISCUSSION OF RESULTS

The activity coefficients for the components were calculated from the experimental data using the well-known relation

$$\gamma_i = \frac{y_i p_t}{x_i p_i} \tag{1}$$

wherein the vapor phase nonideality is considered negligible. Using the Van Ness (*14*) expression, the calculated contribution of the vapor phase nonideality to activity coefficient for *n*-hexane was approximately 0.2%. Neglect of this effect is estimated to introduce an error of less than 1.0% in the activity coefficients for the olefins. The relative volatilities and selectivities were calculated using Equations 2 and 3, respectively:

$$\alpha_{12} = \frac{y_1 x_2}{x_1 y_2} \tag{2}$$

$$S_{12} = \frac{\gamma_1}{\gamma_2} \tag{3}$$

Selected points of vapor-liquid equilibrium data were obtained at 400 and 760 mm. for the ternary systems: DMF–hexane–hexene-1; DMF–hexane–4M1P; and DMF–