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Relative Volatility of Hexane-C$_6$ Olefin Systems in *N*,*N*-Dimethylformamide

R. N. HOLLENSHEAD and MATTHEW VAN WINKLE
University of Texas, Austin, Tex.

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–

Table I. Physical Properties of Materials

	n-Hexane (2)	Hexene-1 (2)	2-M-1-Pentene (*10*)	4-M-1-Pentene (2)	Dimethyl-formamide (*1*)
Molecular weight	86.17	84.16	84.16	84.16	73.09
Normal boiling point, ° C.					
Lit.	68.74	63.48	62.08	53.88	153.4
Exptl.					152.9(*13*)
Exptl.	68.6	63.4	62.1	53.7	152.7
Refractive index, n_D^{25}					
Lit.	1.37226	1.38502	1.38926	1.3799	1.4265
Exptl.	1.37238	1.38514	1.38999	1.38011	1.42817
Density, grams/cc., 25° C.	0.6594	0.6685	0.6798	0.6594	0.945
Antoine constants:[a]					
A	6.87776	6.86572	6.78712[b]	6.87757	7.02722[b]
B	1171.53	1152.971	1122.84[b]	1130.0	1472.504[b]
C	224.366	225.849	225.4[b]	229.0	202.47[b]

[a] $\text{Log } p = A - [(B)/(c + t)]$; p = mm. of mercury, t = ° C. [b] Calculated from experimental data determined by the authors.

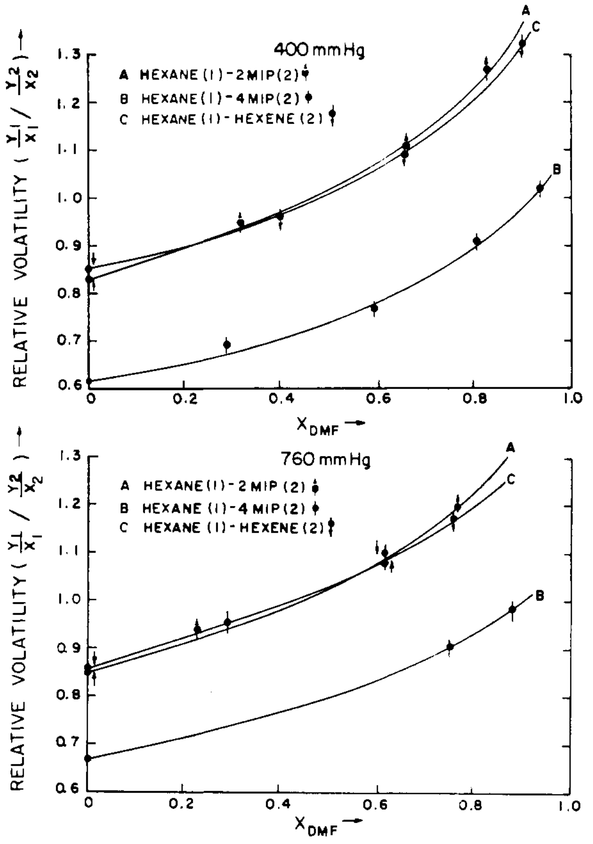

Figure 1. Variation of relative volatility with DMF concentration at 400 and 760 mm. of Hg

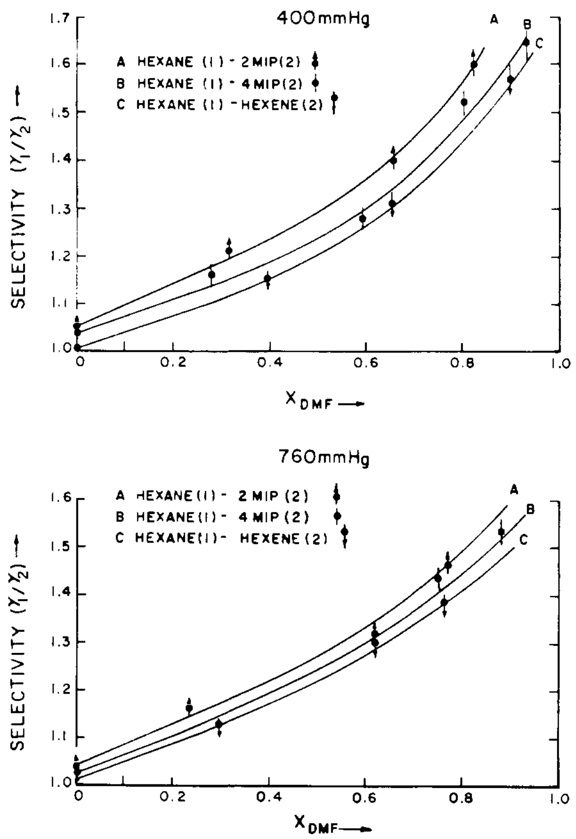

Figure 2. Variation of selectivity with DMF concentration at 400 and 760 mm. of Hg

hexane–2MIP, and the experimental and calculated results are presented in Table II. The relative volatility and selectivity curves are also shown in Figures 1 and 2 for the three systems as a function of solvent concentration. All three systems show a similar upward trend in selectivity with increasing DMF concentration. The downward displacement of the relative volatility curve of the 4MIP–hexane system is a result of the higher vapor pressure of 4MIP relative to that of the other compounds. Since the ratio of the activity coefficients of hexane to olefin is similar for any fixed DMF concentration, the relative volatilities at that that DMF concentration are essentially the ratios of the vapor pressures at that temperature. For example, at 60° C. the ratios of the vapor pressure of hexane with that of the olefins, hexene-1, 2MIP, and 4MIP are, respectively, 0.845, 0.806, and 0.620. This shows that, while increasing the DMF concentration can raise the relative volatility about 70%, the increase would actually be detrimental for separation of hexane and 4MIP, because the relative volatility approaches unity.

The estimated possible cumulative errors in the relative volatility and selectivity values are estimated to be ±2.0% of the calculated values.

A recent correlation which predicts activity coefficients at infinite dilution in polar solvents has been proposed by Weimer and Prausnitz (*15*). This method attempts to

Table II. Vapor-Liquid Equilibrium Data

P, Mm.	T, ° C.	y_1	y_3	x_1	x_3	γ_1	γ_2	γ_3	α_{12}	S_{12}
Hexane(1)-2M1P(2)-DMF(3)										
400.6	47.2	0.636	0.0	0.681	0.0	1.02	0.98	...	0.82	1.04
400.1	47.0	0.634	0.0	0.676	0.0	1.03	0.98	...	0.83	1.06
399.6	48.3	0.626	0.043	0.456	0.315	1.44	1.19	3.84	0.95	1.21
403.6	49.3	0.640	0.043	0.220	0.659	2.97	2.12	1.76	1.11	1.40
403.7	51.8	0.644	0.049	0.110	0.824	5.48	3.42	1.38	1.27	1.60
757.5	66.2	0.638	0.0	0.677	0.0	1.02	0.98	...	0.84	1.04
758.4	68.1	0.611	0.062	0.513	0.229	1.21	1.05	5.33	0.94	1.16
759.5	69.3	0.625	0.065	0.252	0.613	2.43	1.84	1.97	1.08	1.32
759.8	71.8	0.627	0.072	0.148	0.766	3.84	2.63	1.56	1.20	1.46
Hexane(1)-4M1P(2)-DMF(3)										
401.2	44.4	0.601	0.0	0.708	0.0	1.03	0.99	...	0.62	1.05
403.2	44.4	0.594	0.0	0.705	0.0	1.03	1.00	...	0.61	1.03
401.8	46.0	0.613	0.044	0.505	0.279	1.34	1.16	4.98	0.69	1.16
401.3	46.2	0.613	0.045	0.287	0.591	2.43	1.90	2.42	0.77	1.28
400.2	47.0	0.626	0.043	0.133	0.803	5.17	3.41	1.59	0.91	1.52
402.8	64.3	0.596	0.101	0.044	0.934	8.34	5.08	1.35	1.02	1.64
758.5	62.7	0.598	0.0	0.698	0.0	1.03	1.00	...	0.67	1.03
756.3	65.3	0.588	0.065	0.479	0.301	1.36	1.09	4.87	0.78	1.25
762.5	68.2	0.610	0.067	0.170	0.749	3.67	2.57	1.76	0.90	1.43
761.0	75.4	0.605	0.083	0.080	0.879	6.16	4.02	1.34	0.98	1.53
Hexane(1)-Hexene(2)-DMF(3)										
400.3	47.8	0.674	0.0	0.708	0.0	1.02	1.00	...	0.85	1.02
400.9	47.8	0.671	0.0	0.709	0.0	1.01	1.01	...	0.84	1.00
400.5	49.3	0.653	0.058	0.423	0.397	1.56	1.36	3.86	0.96	1.15
399.6	49.3	0.659	0.061	0.236	0.654	2.82	2.15	2.44	1.09	1.31
398.1	59.3	0.621	0.072	0.061	0.899	7.21	4.61	1.27	1.32	1.57
759.8	66.7	0.635	0.0	0.669	0.0	1.01	1.00	...	0.86	1.01
759.6	68.6	0.603	0.075	0.470	0.292	1.29	1.15	4.94	0.95	1.12
760.7	69.7	0.625	0.065	0.247	0.618	2.46	1.90	1.92	1.10	1.30
760.2	71.7	0.627	0.069	0.153	0.759	3.73	2.71	1.53	1.17	1.38

separate the hydrocarbon-solvent interactions into various parts—dispersion, dipole-dipole, induction, and size effects. Through consideration of the above effects, their Equation 10 relates the activity coefficient of a hydrocarbon at infinite dilution in a solvent.

$$RT \ln \gamma_1^\infty = v_1[(\lambda_3 - \lambda_1)^2 + \tau_3^2 - 2\psi_{13}] + RT\left(\ln \frac{v_1}{v_3} + 1 - \frac{v_1}{v_3}\right) \tag{4}$$

The subscript 1 refers to the hydrocarbon and subscript 3 to the solvent. By combining the above equation with that for another component, the following equation results:

$$RT \ln S_{12}^\infty = v_1[(\lambda_3 - \lambda_1)^2 + \tau_3^2 - 2\psi_{13}] - v_2[(\lambda_3 - \lambda_2)^2 + \tau_3^2 - 2\psi_{23}] + RT\left(\ln \frac{v_1}{v_2} + \frac{v_2 - v_1}{v_3}\right) \tag{5}$$

All the above parameters (v, λ, τ. ψ) are determined from pure component data except the interaction term, ψ. This term has been correlated as a function of the polar solubility parameter, τ, for the solvent and the class of the hydrocarbon (paraffin, olefin, or aromatic). To obtain the solubility parameters, the total energy of vaporization is divided into two parts—one resulting from the nonpolar interactions, and the other including the dipole and induction effects.

$$\frac{\Delta U_3}{v_3} = \frac{\Delta U_3\ (\text{nonpolar})}{v_3} + \frac{\Delta U_3\ (\text{polar})}{v_3} \equiv \lambda_3^2 + \tau_3^2 \tag{6}$$

For the hydrocarbons, the polar contribution is zero, and the nonpolar solubility parameter, λ, is given by:

$$\lambda_1^2 = \frac{\Delta U_1}{v_1} \tag{7}$$

The contribution to the energy of vaporization of a polar molecule due to the nonpolar effects is found by considering the energy of vaporization of the molecule's "homomorph." The homomorph of a molecule is the equistructural hydrocarbon at the same reduced temperature. Graphs prepared by Weimer and Prausnitz allow consideration of the homomorph at the same molar volume as well as reduced temperature. The nonpolar solubility parameter is calculated using the energy of vaporization of the homomorph in Equation 7. The polar solubility parameter is calculated by Equation 6 using the total energy of vaporization calculated from vapor pressure data. The above parameters are tabulated (*15*) for some solvents and hydrocarbons at various temperatures. The selectivities obtained by extrapolation of the experimental data, $x_3 \xrightarrow{\text{limit}} 1.0$ S_{12}, are compared with those calculated with the above correlation in Table III. The excellent agreement would indicate that the correlation may be a reliable means for preliminary screening of various solvents for initial design considerations.

The results of this investigation show that DMF could serve as an extractive distillation solvent for the separation

Table III. Comparison of Calculated and Extrapolated Experimental Selectivities at Infinite Dilution

	400 mm. (130° C.)		760 mm. (153° C.)	
System	S_{12}^∞ calcd.[a]	S_{12}^∞ exptl.	S_{12}^∞ calcd.[a]	S_{12}^∞ exptl.
Hexane-Hexene-1	1.68	1.70 ± 0.05	1.65	1.63 ± 0.05
Hexane-4M1P	1.87	1.75 ± 0.1	1.81	1.68 ± 0.1
Hexane-2M1P	1.90	1.85 ± 0.1	1.87	1.80 ± 0.1

[a] Calculated from the correlation by Weimer and Prausnitz using data in article (*15*), if given. The parameters for 4M1P and 2MiP were estimated using data from (*2*) and vapor pressure data.

of the hexane-hexene system, and for the hexane-2M-1 pentane system if more than about 0.85 mole fraction of DMF were used, but would be relatively ineffective in separating the C_6 isomeric olefins studied in this investigation. The similarity in the behavior of the three systems seems to indicate that the enhancement of the selectivity results almost entirely from the interactions of DMF with the olefin bond. The highest selectivity was found in the hexane-2M1P-DMF system; 2M1P has the smallest molar volume (124 cc. per mole) and has the methyl group located adjacent to the double bond. The selectivity for 4M1P (128 cc. per mole) is slightly larger than that for hexane-1 (126 cc. per mole) even though hexene-1 has a slightly smaller molar volume. Thus, the position of the methyl group must have a slight effect on the interaction and the related selectivity.

The selectivity and relative volatility are lower at the higher pressure for all systems studied, as would be expected, since the equilibrium temperature was increased about 15° C.

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The System o-Nitroaniline–2,4-Dinitroaniline

LOHR A. BURKARDT
Chemistry Division, U. S. Naval Ordnance Test Station, China Lake, Calif.

No evidence of complex formation was found for the system o-nitroaniline–2,4-dinitroaniline. The eutectic contains 14.5 mole of 2,4-dinitroaniline and melts at 60.7° C.

In THE COURSE of studies of the polymorphism of *o*-nitroaniline, knowledge of the phase diagram of the system *o*-nitroaniline–2,4-dinitroaniline became desirable. Since this system does not appear to have been previously investigated, a study was undertaken using an apparatus (*1*) which permits a stepwise approach to the liquidus point. Solid-liquid equilibrium was demonstrated at each thermal step by constancy of the light transmission of the sample.

The *o*-nitroaniline was recrystallized five times from a mixture of equal volumes of ethyl alcohol and water, and then vacuum-dried; the melting point was 70.6° C. The 2,4-dinitroaniline was recrystallized from hot ethyl alcohol and vacuum-dried; the melting point was 179.9° C.

Because of the rather deep color of melts of these materials, the apparatus was modified slightly. A stirrer was used, similar in general shape to that described (*1*), but having a solid glass plate with plane sides instead of a hole for the light to pass through. This arrangement reduced the amount of melt through which the light had to pass.

Six-gram samples of the required compositions were melted and stirred thoroughly. The temperature of the sample was allowed to fall until a small amount of solid was formed, then was raised stepwise; the sample was held at each temperature until the light transmission of the sample became constant. Unfortunately, the light transmission of the sample becomes very erratic just as the liquidus point is being reached, because of the small number of solid particles in the light beam. The liquidus was then approached by raising the bath temperature in 0.1° C. steps. The temperature was held constant for about 15 minutes at each step and the behavior of the solid particles, which were strongly illuminated, was followed visually. The temperature step at which solids were no longer visible at the end of the 15-minute period was taken as the liquidus temperature. Attempts at prolonging the time of holding the sample at the step immediately before complete solution of the solids led to some darkening of the sample, suggesting possible degradation of the sample. Such an effect could introduce a larger and more variable error than would be made by assuming the true liquidus temperature to be between the complete solution temperature step immediately preceding it. In this case the accuracy of the determination might be best expressed as the complete solution temperature, +0.0° to 0.1° C.

The melting point of the eutectic was obtained by heating the completely solid sample through the eutectic melting point with temperature gradients of approximately 0.1° between the bath and sample. With such temperature gradients, a flat is obtained at the eutectic melting point.

No evidence of complex formation was found for this