NOMENCLATURE

∂ = differential operator
m = mass, grams
n = number of moles
P = pressure, atm
T = temperature, °K
ε (calor) = heat equivalent of calorimeter, cal/°K
ε (cont) = heat equivalent of contents, cal/°K
ΔE_{dec} = energy of decomposition, cal
ΔE_{ign} = electrical ignition energy, cal
$\Delta E_{\text{cor to std states}}$ = energy for reduction to standard states, cal
$\Delta Ec°$ = standard energy of idealized combustion reaction, kcal/mol
$\Delta Hc°$ = standard enthalpy of combustion, kcal/mol
$\Delta Hf°$ = standard enthalpy of formation, kcal/mol
$\Delta Hv°$ = standard enthalpy of vaporization, kcal/mol

SUBSCRIPTS

i = initial state
f = final state

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Phase Studies of Some Nitroalkane Hydocarbon Mixtures

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Upper critical solution temperatures were determined for the solutions nitroethane–*n*-decane, ~58°C; nitroethane–*n*-nonane, 49.5°C; nitroethane–*n*-hexane, 32.5°C; nitroethane–cyclohexane, 25°C; nitroethane–methylcyclohexane, 25°C; 2-nitropropane–*n*-nonane, —4.5°C; nitromethane–1,3,5-trimethylbenzene, —16°C; and nitromethane–1,2,4-trimethylbenzene, —31°C. No liquid-liquid immiscibility was observed in benzene solutions of nitromethane, nitromethane-d_3, nitroethane, 1-nitropropane, or 2-nitropropane. The benzene–2-nitropropane system was determined to be a simple eutectic at a temperature of —98°C and composition of 0.93 mole fraction 2-nitropropane. Cooling curve measurements on benzene solutions of nitromethane and nitromethane-d_3 indicate they form simple eutectics.

Several cases of liquid-liquid immiscibility were observed in connection with our work on the excess Gibbs energy of mixing (*1*) and on the surface tension of nitroalkane–hydrocarbon solutions. This paper reports an extension of these observations to eight nitroalkane hydrocarbon solutions for which upper critical solution temperatures (UCST) were determined. Also reported are some freezing and eutectic temperatures determined from cooling curves of solutions of benzene with nitromethane, nitromethane-d_3, and 2-nitropropane.

EXPERIMENTAL

Chemicals. The nitroalkanes were purified by drying over calcium sulfate followed by distillation under reduced pressure. Nitromethane, Fisher reagent grade, distilled at 60°C and 183 torr; nitroethane, Matheson, Coleman and Bell practical grade, distilled at 57°C and 97 torr, 2-nitropropane, Eastman practical grade distilled at 60°C and 100 torr. Boiling points and densities checked satisfactorily with literature values (*13*). Nitromethane-d_3, Dia-

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prep, Inc., 99% minimum isotopic purity was used as received. *n*-Hexane, Phillips 99 mol %, cyclohexane, Fisher, and methylcyclohexane, Phillips 99 mol % were each shaken with concentrated H_2SO_4, washed with water until neutral to litmus, dried over $CaSO_4$, and distilled at atmospheric pressure from CaH_2. 1,3,5-Trimethylbenzene, Eastman practical grade, was dried over $CaSO_4$ and distilled once from CaH_2 and a second time from over sodium at 79°C and 42 torr. Hydrocarbon boiling points and densities checked satisfactorily with literature values (*10*).

n-Nonane and *n*-decane, both Phillips 99 mol %, benzene, Fisher ACS certified, and 1,2,4-trimethylbenzene, Phillips research grade, 99.89 mol % were used as received.

Determination of Liquid-Liquid Immiscibility. The nitroalkane–alkane and cycloalkane solutions were prepared by weight from glass syringes in 13 × 100 mm Kimax screw cap culture tubes and sealed by a cap with a Teflon-faced rubber liner. The tubes were suspended in a 3-liter well-stirred water bath and cloud points observed visually. At least two observations were made of each set of samples, the first at a relatively fast cooling rate to find the approximate cloud point temperature and the second at a slow cooling rate to more precisely determine the cloud point temperature. Temperatures were observed on a 0.1 degree graduated mercury in a glass thermometer whose calibration had been checked at the ice point. The cloud point temperatures were reproducible to better than ±0.1° and are recorded in Table I to the nearest 0.1°C.

The solutions of nitromethane with the two aromatic hydrocarbons 1,2,4- and 1,3,5-trimethylbenzene were sealed in 5-ml glass vials. The cloud points were observed visually in an acetone bath slowly cooled by the addition of portions of dry ice. Temperatures were observed on a +20 to −100°C alcohol thermometer and are reproducible to ±3°, in part because of uneven temperature distributions in the acetone–dry ice bath.

Determination of Freezing and Eutectic Temperatures. Cooling curves were run on a Precision Scientific Co. freezing point apparatus equipped with a Leeds and Northrup Co. Mueller bridge and platinum resistance thermometer. The minimum sample size was 50 ml. Usually a nitroalkane–benzene solution was prepared, a cooling curve taken, a known amount of nitroalkane added, and a second cooling curve taken. The procedure was then repeated with a new sample. Only ordinary precautions were taken to exclude water from the system. Either dry ice-acetone or liquid nitrogen was used as the coolant around the evacuated Dewar flask holding the sample.

Table I. Cloud Point Temperatures for Some Nitroparaffin-Hydrocarbon Mixtures

Nitromethane(1)–
1,2,4-trimethylbenzene(2)

X_1	T, °C
0.25	−65
0.33	−60
0.44	−44
0.66	−33
0.74	−31
0.88	−40

Nitromethane(1)–
1,3,5-trimethylbenzene(2)

X_1	T, °C
0.30	−43
0.38	−33
0.39	−29
0.51	−21
0.59	−18
0.70	−16
0.79	$-16^{1}/_{2}$
0.90	−25

Nitroethane(1)–
n-decane(2)

X_1	T, °C
0.730	58

Nitroethane(1)–
n-nonane(2)

X_1	T, °C
0.315	42.4
0.460	48.9
0.605	49.5
0.715	49.1
0.810	45.8
0.875	37.9
0.940	16.3

Nitroethane(1)–
n-hexane(2)

X_1	T, °C
0.265	28.6
0.415	32.4
0.545	32.1
0.650	31.8
0.750	25.9
0.830	15.4
0.910	<0

Nitroethane(1)–
cyclohexane(2)

X_1	T, °C
0.220	24.1
0.365	24.8
0.495	24.6
0.605	23.2
0.710	18.1
0.815	5.4
0.900	<0

Nitroethane(1)–
methylcyclohexane(2)

X_1	T, °C
0.135	8.8
0.235	18.0
0.380	24.3
0.500	24.9
0.625	24.2
0.755	16.9
0.870	<0

2-Nitropropane(1)–
n-nonane(2)

X_1	T, °C
0.425	−4.8
0.550	−4.6
0.680	−5.3
0.775	−7.8
0.865	−19.1

RESULTS AND DISCUSSION

Results of the determination of upper critical solution temperatures (UCST) of various nitromethane–hydrocarbon solutions (*2*, *5*–*7*), nitroethane-isooctane (UCST 29.8°C) (*14*), and nitroethane-3-methylpentane (UCST 26.46°C) (*16*) are in the literature. Several generalizations about nitromethane–hydrocarbon UCST have been stated. The UCST of nitromethane with alkanes appear at temperatures well above room temperature while the UCST with aromatics appears near or below room temperature (*6*, *7*). For nitromethane alkane solutions, the UCST and nitroalkane mole fraction increase as the normal chain alkane molecular weight increases, and branched chain alkanes appear to have a lower UCST than the corresponding normal chain alkane with a given nitroalkane (*5*).

The cloud point temperatures and compositions for the solutions showing liquid-liquid immiscibility are given in Table I and shown in Figure 1. In general, the results conform to the trends stated above. The nitroethane–alkane UCST behavior appears to parallel that reported for the nitromethane–alkane solutions (*5*), but at temperatures 65–70° lower for the same alkane. The pattern may repeat for 2-nitropropane which becomes partially miscible with *n*-nonane about 55° lower in temperature than does nitroethane.

Reports (*4*, *12a*) of liquid-liquid immiscibility in nitromethane–benzene solutions were not confirmed. However, liquid-liquid immiscibility was observed in solutions of nitromethane with 1,2,4-trimethylbenzene (pseudocumene) at −31°C and with 1,3,5-trimethylbenzene (mesitylene) at −16°C. The results are consistent with earlier reports (*6*, *7*) of no immiscibility in these two solutions down to −20°C, but they do not agree with a report (*2*) of UCST of +1°C for nitromethane–1,2,4-trimethylbenzene solutions.

Solutions of nitroethane with 1,2,4-trimethylbenzene and with 1,3,5-trimethylbenzene and of 2-nitropropane with 1,3,5-trimethylbenzene showed neither freezing nor liquid-liquid immiscibility down to ∼−60°C.

Freezing and eutectic temperatures were obtained from cooling curves of 2-nitropropane–benzene solutions (Table II). The solid-liquid phase diagram (Figure 2) is a simple eutectic with an eutectic temperature of −98°C and composition 0.93 mole fraction 2-nitropropane.

The cooling curves run on benzene solutions of nitromethane and nitromethane-d_3 indicate both solutions form simple eutectics. The nitromethane–benzene freezing and eutectic temperatures of this work are compared in Figure 2 with values from an earlier report (*12b*). The experimental details of the earlier work are not available. The agreement is fair

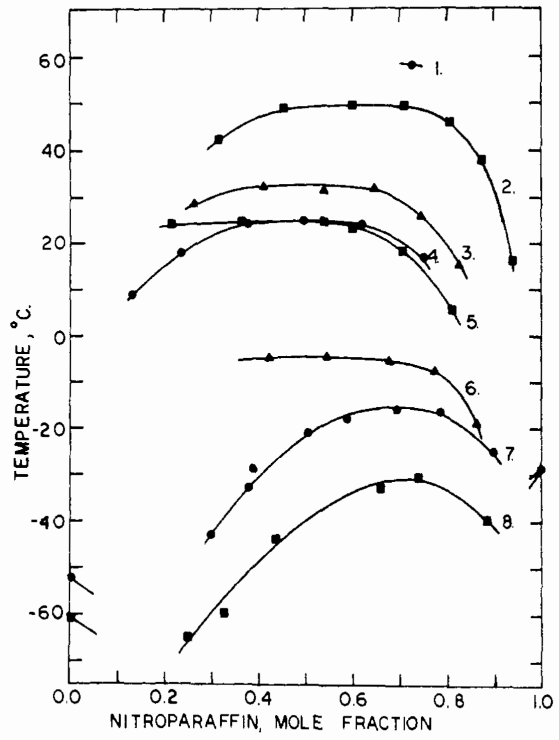

Figure 1. Phase diagram: cloud point temperature vs. mole fraction nitroparaffin

1. Nitroethane–n-decane
2. Nitroethane–n-nonane
3. Nitroethane-n-hexane
4. Nitroethane–Methylcyclohexane
5. Nitroethone–cyclohexane
6. 2-Nitropropane–n-nonane
7. Nitromethane–1,3,5-trimethylbenzene
8. Nitromethane–1,2,4-trimethylbenzene

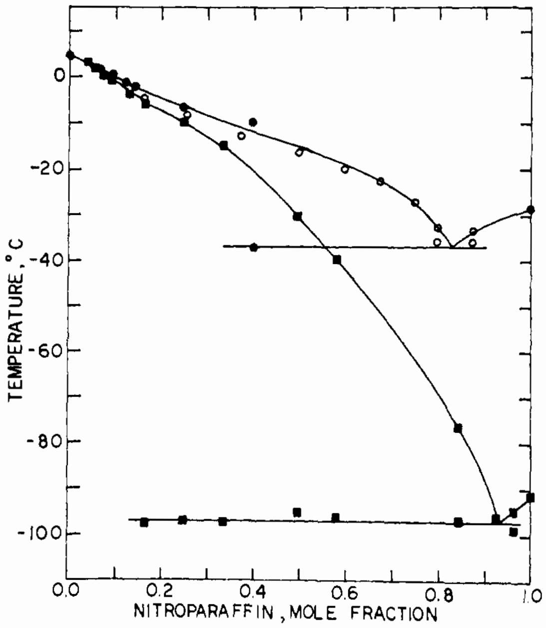

Figure 2. Phase diagram: freezing and eutectic temperatures vs. mole fraction nitroparaffin

● Nitromethane–benzene, this study
○ Nitromethane–benzene, ref. *12b*
■ 2-Nitropropane–benzene

with the eutectic temperatures agreeing within a degree, but the freezing points reported here are several degrees higher throughout the composition region of common measurement. The nitromethane-d_3 freezes 0.5° below nitromethane, but the nitromethane–benzene eutectic temperature is 2.5° higher for the deuterium than the hydrogen compound. The nitromethane–benzene system may be an example of a submerged miscibility gap (*9*). The presence of a small amount of a polar third component can cause nitromethane–benzene immiscibility. For example, less than 0.5 vol % water causes immiscibility in a 50-50 vol % nitromethane–benzene solution at 0°C.

Qualitative studies of benzene solutions of nitroethane and 1-nitropropane indicate that they are also simple eutectic systems.

Cryoscopic studies may be used to elucidate the extent and nature of association of a highly polar compound, as the nitroalkanes, in a nonpolar solvent such as benzene (*8*). One can distinguish between nitroalkane dimer formation

$$2A \rightleftarrows A_2 \qquad (1)$$

and a chain association

$$A + A_i \rightleftarrows A_{i+1} \qquad (2)$$

which may contain a variable number of monomer molecules if one can assume unit activity of monomer and association complexes and if the equilibrium constants are almost independent of i, the number of monomer units in the chain. The equilibrium constants may be calculated from cryoscopic measure-

Table II. Freezing and Eutectic Temperatures of Some Nitroparaffin Benzene Solutions

Nitromethane(1)-benzene(2)			Nitromethane-d_3(1)-benzene(2)			2-Nitropropane(1)-benzene(2)		
X_1	Fp, °C	E, °C	X_1	Fp, °C	E, °C	X_1	Fp, °C	E, °C
0.0	5.45	...	0.0	5.45	...	0.0	5.45	...
0.0654	1.59	...	0.0609	2.07	...	0.0374	3.06	...
0.0942	0.30	...	0.116	− 0.68	...	0.0553	2.00	...
0.123	− 1.41	...	0.275	− 7.94	−34.7	0.0721	0.31	...
0.142	− 2.29	...	0.780	−26.03	−34.6	0.090	− 0.80	...
0.248	− 6.86	...	1.000	−28.96	...	0.129	− 3.92	...
0.397	− 9.86	−37.2				0.165	− 5.72	−97.9
1.000	−28.50	...				0.249	− 9.89	−97.2
						0.335	−14.84	−97.4
						0.497	−30.13	−95.4
						0.581	−39.66	−96.3
						0.845	−76.52	−96.9
						0.924	−96.11	...
						0.962	−94.97	−98.4
						1.000	−91.50	...

Table III. Comparison of Equilibrium Constants for Dimer and for Chain Formation of Nitroparaffins in Benzene

X_1	ΔT	ϕ	K_{dimer}	K_{chain}
		Nitromethane-d_3(1)–Benzene(2)		
0.02	1.18	0.894	8.6	6.6
0.04	2.30	0.866	6.3	4.5
0.06	3.40	0.848	5.3	3.5
0.08	4.45	0.827	5.1	3.2
0.10	5.40	0.796	5.8	3.2
0.12	6.30	0.768	6.7	3.3
		Nitromethane(1)–Benzene(2)		
0.02	1.21	0.917	6.0	5.0
0.04	2.35	0.885	4.9	3.7
0.06	3.47	0.865	4.2	3.0
0.08	4.55	0.845	4.1	2.7
0.10	5.63	0.831	3.9	2.5
0.12	6.69	0.817	3.8	2.2
0.14	7.70	0.800	4.0	2.2
0.16	8.70	0.785	4.1	2.2
0.18	9.65	0.768	4.5	2.2
		2-Nitropropane(1)–Benzene(2)		
0.02	1.32	1.000	−0.02	0.02
0.04	2.62	0.987	0.33	0.32
0.06	3.96	0.989	0.19	0.18
0.08	5.35	0.997	0.04	0.04
0.10	6.78	1.005	−0.05	0.05
0.12	8.30	1.020	−0.15	0.16
0.14	9.94	1.042	−0.25	0.27
0.16	11.61	1.059	−0.30	0.33
0.18	13.05	1.051	−0.24	0.26

ments by the following equations. For dimer formation, Equation 1

$$K_{\text{dimer}} = (1 - \phi)/(2\phi - 1)^2 X_1 \tag{3}$$

and for chain association, Equation 2

$$K_{\text{chain}} = (1 - \phi)/\phi^2 X_1 \tag{4}$$

where ϕ is the osmotic coefficient defined as

$$\phi = -(\Delta H_f/RT_f)(\Delta T/T)/\ln X_1 \tag{5}$$

ΔH_f = the heat of fusion of benzene, 2351 cal mole^{-1} (*10*)
T_f = the benzene freezing point
T = the solution freezing point
ΔT = the freezing point depression
X_1 = the mole fraction of nitroalkane calculated as a monomer
$1/\phi$ = the average degree of association

Large-scale plots of the freezing point–composition curves were prepared and values of ΔT read off at 0.02 mole-fraction intervals from 0–0.18 mole fraction nitroalkane for the three nitroalkane–benzene solutions. Values of K_{dimer} and K_{chain} were calculated from Equations 3 and 4. The results (Table III) allow no definite conclusion to be drawn about the nature of the association of the nitroalkanes in benzene solution. The negative values of K_{dimer} for 2-nitropropane causes one to favor the chain-type association for 2-nitropropane. It does appear that nitromethane and 2-nitropropane associate to a different degree in benzene and this is in accord with the excess Gibbs energy measurements on these solutions at 30°C (*1*). The value of the nitromethane dimerization constant in benzene is in reasonable agreement with the value of 9.54 at 20°C reported for the nitromethane dimerization constant in carbon tetrachloride from an ultraviolet spectra study (*11*).

A model which assigns all the nitroalkane–aromatic hydrocarbon freezing-point abnormality to association of the nitroalkane is probably too simple. There is spectroscopic evidence for association of both aromatic (*3*) and alkane (*15*) nitro compounds with aromatic hydrocarbons. A model to explain the nonideal behavior in these solutions will have to take into account the competitive association of nitroalkane for nitroalkane and nitroalkane for aromatic hydrocarbon.

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