Solubility of Nitroethane in Hydrocarbons

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Mutual solubility data have been determined for seven binary and two ternary nitroethane-hydrocarbon systems using the phase equilibrium and cloud point methods. The hydrocarbons used in the binary studies were: *n*-hexane, 2-methylpentane, 1-hexane, *n*-octane, 2,2,4-trimethylpentane, 1-octene, and *n*-decane. Mutual solubility data for the binary systems were determined at various temperatures up to the critical solution temperature. The ternary systems studied were nitroethane–*n*-octane at 0° and 25° C. and nitroethane–*n*-octane–2,2,4-trimethylpentane at 35° C.

NITROPARAFFINS have miscibility characteristics similar to furfural and other organic solvents used in petroleum extraction. The consideration that nitroparaffins might have potential use in the petroleum extraction field initiated this study of phase equilibria. A series of qualitative tests was carried out to ascertain the possible occurrence of partial miscibility in 52 binary nitroparaffin–hydrocarbon systems in a temperature range from −15° to 30° C. (*3*). These tests include 13 hydrocarbons (*n*-pentane, *n*-hexane, 2-methylpentane, 1-hexene, cyclohexane, cyclohexene, *n*-heptane, *n*-octane, 2,2,4-trimethylpentane, 1-octene, *n*-decane, benzene, and toluene) and four nitroparaffins (nitromethane, nitroethane, 1-nitropropane, 2-nitropropane). From these tests certain generalities were observed: for a given nitroparaffin, the critical solution temperature increased as the number of carbon atoms in the straight chain saturated aliphatic hydrocarbon increased; for hydrocarbons containing the same number of carbon atoms, the critical solution temperature decreased in the following order: normal paraffin, isomers of normal paraffin, saturated cyclic hydrocarbon, and unsaturated hydrocarbons; for a given hydrocarbon, the critical solution temperature decreased as the number of carbon atoms in the nitroparaffin increased. These generalities suggested that some of the lower nitroparaffins such as nitromethane or nitroethane can be used to separate hydrocarbons of different structure and/or molecular weight.

A literature survey revealed a paucity of quantitative mutual solubility data for nitroparaffin-hydrocarbon systems. This article presents mutual solubility data for seven binary and two ternary nitroethane–hydrocarbon systems. The mutual solubility data were determined at various temperature intervals up to the critical solution temperature. The hydrocarbons used in the binary studies (*3*) were: *n*-hexane, 2-methylpentane, 1-hexene, *n*-octane, 2,2,4-trimethylpentane, 1-octene, and *n*-decane. The ternary systems studied (*5*) were nitroethane–*n*-octane–*1*-octene, and nitroethane–*n*-octane–2,2,4-trimethylpentane. The reader is referred elsewhere (*3*, *5*) for experimental details and further discussion.

EXPERIMENTAL

Materials. All the hydrocarbons used in this study had a purity of better than 99 mole % as stated by the supplier. This was supported by both refractive index and gas chromatographic analysis. The nitroparaffins were reported by the supplier to be better than 96 mole % pure. The nitromethane used had a purity of 99 mole %. The nitroethane was reported to contain 3.9% of 2-nitropropane. Analysis of the nitroethane by gas chromatograph confirmed the presence of 2-nitropropane. The materials were used without further purification.

Procedure. The data for the binary and ternary mixtures studied were obtained by the synthetic (cloud-point) and analytical (phase equilibrium) methods as described by Vold and Vold (*7*). The cloud point was easily detected for the binary systems studied. For the ternary systems the cloud point was determined by titrating a third component into binary samples of known composition in a constant temperature bath. In the case of the two ternary mixtures, no distinct change in the transparency of the clear mixture was observed to indicate to the unaided eye that the cloud point had been obtained; only the presence of finely dispersed globules of the second phase, which were visible through a magnifying glass, denoted the fact that the cloud point had been reached.

The analytical method consisted of withdrawing a sample from each of the coexisting phases (for either the binary or ternary mixtures) from an equilibrium cell in a constant temperature bath, and analyzing the samples by gas chromatographic techniques. The temperature of the bath was controlled to ±0.05° C. The commonly used refractive index method of analysis could not be applied to these systems because nitroethane and the hydrocarbons studied do not have a sufficiently large difference in their refractive index values.

Analysis of the equilibrium liquid phases was carried out by means of a Model 154B Vapor Fractometer (Perkin-Elmer Corp., Norwark, Conn.) using helium as the carrier gas. Complete resolution of all binary systems studied,

Table I. Comparison of Mutual Solubility of Nitromethane–Cyclohexane System

Source of Data	Weight Fraction of Cyclohexane in Hydrocarbon-Rich Phase			Weight Fraction of Cyclohexane in Nitromethane-Rich Phase		
	15° C.	25° C.	30° C.	15° C.	25° C.	30° C.
Weck and Hunt (*9*)		0.978			0.051	
This work						
Gas chromatograph	0.978			0.043	0.053	0.065
Index of refraction	0.978	0.972	0.966	0.043	0.054	0.066

except the nitroethane–*n*-octane and nitroethane–1-octene systems, was obtained using two commerically available 2-meter diisodecyl phthalate columns (Perkin-Elmer A column) in series at approximately 150° C. Analysis of the latter two systems was carried out at 86° to 87° C. using a specially prepared 6-foot triethylene glycol–silver nitrate column (*4*) followed by a 2-meter diisodecyl phthalate column.

The compositions of the phases in the ternary nitroethane–1-octene–*n*-octane system were determined using a 30-inch dimethylsulfolane column operated at 40° C. Analysis of the ternary nitroethane–*n*-octane–2,2,4-trimethylpentane system was carried out using a polyethylene glycol (Carbowax 1500) column (Perking-Elmer K column) followed by a 2-meter diisodecyl phthalate column (Perkin-Elmer A column). These columns were operated at 108° C.

For the binary and ternary composition determinations, calibration curves were prepared for the gas chromatograph using mixtures of known composition. These curves consisted of a plot of the ratio, *R*, of the peak height of a given component by the sum of the peak heights of all of the components *vs.* weight fraction for fixed column temperature and pressure. This ratio was found to be relatively insensitive to sample size but dependent upon column operating conditions. Samples of known composition were introduced periodically to check the reproducibility of the measurements.

Results. To check the experimental procedure used in the phase equilibrium method of determining mutual solubility, the nitromethane–cyclohexane system was studied at 15°, 25°, and 30° C. Analysis of the phases was made both by gas chromatograph and by means of the index of refraction. The results obtained are compared with the published data of Weck and Hunt (*9*) in Table I.

The agreement with the data of Weck and Hunt is within the estimated error of the two studies.

The mutual solubility data for the seven binary systems studied are given in Table II. The uncertainty in the experimental results for six of the binary systems was estimated to be ±0.002 weight fraction for the analytical (phase equilibrium) method and ±0.1° C. for the synthetic (cloud-point) method except in the case of the nitroethane–1-hexene system. The reproducibility for the latter system, using the analytical method, was ±0.005 weight fraction. The plotted curves of the mutual solubility *vs.* temperature data were found to be smooth, with good agreement between the data obtained from the analytical and synthetic methods where the temperature range of the data overlapped. Two or more portions of each equilibrium phase sample were analyzed, using the gas chromatograph, to check the reproducibility of the analysis. In most instances a second sample was withdrawn for analysis after the liquid system had been stirred and re-equilibrated at the same temperature. This provided a check on the establishment of equilibrium and the sampling technique.

Vreeland and Dunlap (*8*) have determined the mutual solubility in the nitroethane–2,2,4-trimethylpentane system from 25° C. up to critical solution temperature. The critical solution temperature, 29.5° C., obtained in this work agrees quite closely with the value of 29.8° C. reported by them. Their mutual solubility data (*1*) at 25° C. are 0.314 and 0.778 weight fraction of hydrocarbon. These values may be compared with corresponding values obtained in the present work of 0.279 and 0.774 at 25.01° C. Francis (*2*) has reported the critical solution temperatures of the nitroethane–2,2,4-trimethylpentane, nitroethane–*n*-hexane, and nitroethane–*n*-decane systems to be 29°, 27°, and 50° C., respectively. These temperatures are all slightly lower than those found in this work.

The experimental results obtained for the two ternary systems studied are shown in Table III. Tie-line data are given as upper phase/lower phase compositions. All other

Table II. Experimental Mutual Solubility of Binary Nitroethane–Hydrocarbon Systems

n-Hexane

Temp., °C.	Wt. fraction hydrocarbon
2.90	0.921
	0.101
9.40	0.894
	0.136
13.65	0.876
19.95	0.818
	0.214
24.00	0.769
	0.265
24.1^a	0.7737
25.30	0.743
	0.290
26.1^a	0.3158
26.25	0.734
	0.310
27.20	0.698
	0.324
27.4^a	0.3487
27.8^a	0.6950
28.3^a	0.3837
28.7^a	0.6610
29.2^a	0.4555
29.2^a	0.6017
29.3^a	0.5152
29.3^a	0.5703
29.3	C.S.T.^{b}

2-Methylpentane

Temp., °C.	Wt. fraction hydrocarbon
−0.35	0.137
2.05	0.916
3.80	0.151
6.30	0.899
8,00	0.169
8.75	0.890
10.85	0.186
11.20	0.877
13.70	0.201
13.75	0.857
15.95	0.843
17.80	0.236
19.00	0.812
20.00	0.259
20.25	0.792
21.00	0.782
23.4^a	0.3072
24.00	0.324
24.20	0.716
25.20	0.362
25.3^a	0.6969
25.50	0.680
25.6^a	0.6819
25.8^a	0.3812
26.2^a	0.6594
26.6^a	0.5783
26.6^a	0.6293
26.7^a	0.4241
26.7^a	0.4688
26.7^a	0.5331
26.7	C.S.T.^{b}

1-Hexane

Temp., °C.	Wt. fraction hydrocarbon
−43.0	0.883
	0.212
−38.4	0.857
	0.264
−34.0	0.822
	0.317
−30.0	0.746
	0.410
−29.9^a	0.7295
−29.8^a	0.4081
−29.0^a	0.4650
−28.6^a	0.6411
−28.5^a	0.5602
−28.5	C.S.T.^{b}

1-Octene

Temp., °C.	Wt. fraction hydrocarbon
−27.5	0.915
	0.132
−25.4	0.904
	0.140
−21.6	0.885
	0.162
−19.7	0.875
	0.174
−16.7	0.851
	0.199
−13.0	0.817
	0.235
−11.0	0.791
	0.261
−9.0	0.765
	0.293
−7.8	0.738
	0.312
−6.5^a	0.3650
−5.8^a	0.6901
−4.7^a	0.4503
−4.7^a	0.5009
−4.6^a	0.5884
−4.6	C.S.T.^{b}

2,2,4-Trimethylpenta

Temp., °C.	Wt. fraction hydrocarbon
1.80	0.923
	0.134
5.12	0.913
8.80	0.898
	0.161
11.90	0.885
14.40	0.870
	0.193
17.42	0.851
20.45	0.826
	0.236
21.85	0.814
	0.248
23.63	0.793
	0.268
24.2^a	0.2721
24.6^a	0.7792
25.01	0.774
	0.279
26.0^a	0.2910
26.4^a	0.7411
27.5^a	0.3201
28.3^a	0.6985
28.9^a	0.3711
29.4^a	0.4412
29.4^a	0.6248
29.5^a	0.5051
29.5^a	0.5689
29.5	C.S.T.^{b}

n-Octane

Temp., °C.	Wt. fraction hydrocarbon
4.20	0.941
	0.092
6.50	0.935
	0.097
10.70	0.924
	0.107
14.2^a	0.9143
14.85	0.910
	0.123
16.85	0.901
	0.132
18.40	0.895
	0.137
20.80	0.885
	0.150
21.0^a	0.1500
23.3^a	0.8770
26.0^a	0.1765
28.3^a	0.8451
32.8^a	0.2314
34.6^a	0.7863
39.5^a	0.6912
39.6^a	0.3492
41.3^a	0.5099
41.3	C.S.T.^{b}

n-Decane

Temp., °C.	Wt. fraction hydrocarbon
2.33^c	0.956
7.40^c	0.948
7.80^c	0.057
12.45^c	0.938
13.80^c	0.072
17.20^c	0.084
18.20^c	0.924
21.50^c	0.912
22.40^c	0.096
31.8^a	0.1320
32.4^a	0.8735
39.3^a	0.1738
42.0^a	0.8095
46.8^a	0.2387
48.6^a	0.7380
49.3^a	0.7104
50.8^a	0.3246
50.8^a	0.6670
52.3^a	0.5778
52.4^a	0.4380
52.6^a	0.4753
52.6	C.S.T.^{b}

[a] Obtained by synthetic (cloud-point) method; all other data obtained by the analytical (phase equilibrium) method. [b] Critical solution temperature, obtained by interpolation. [c] Only one of the equilibrium phases was analyzed at each temperature for this system.

Table III. Experimental Data for Ternary Nitroethane–Hydrocarbon Systems.

Nitroethane–*n*-Octane–1-Octene Wt. Fractions at 0.0° ± 0.05° C

Nitroethane	*n*-Octane	Nitroethane	*n*-Octane
0.058	0.942^a	0.291	0.107
0.077	0.718	0.340	0.078
0.079/0.886	0.668/0.083	0.506	0.045
0.099/0.852	0.515/0.070	0.529	0.041
0.126/0.812	0.371/0.065	0.747	0.048
0.152	0.269	0.806	0.057
0.174	0.233	0.832	0.066
0.240	0.155	0.910^a	0.090

Nitroethane–*n*-Octane–2,2,4-Trimethylpentane Wt. Fractions at 25.0° ± 0.05° C.

Nitroethane	*n*-Octane
0.137/0.826	0.786/0.157
0.149/0.797	0.519/0.120
0.168/0.764	0.334/0.085

Nitroethane–*n*-Octane–2,2,4-Trimethylpentane Wt. Fractions at 35.0° ± 0.05° C.

Nitroethane	*n*-Octane	Nitroethane	*n*-Octane
0.718	0.237	0.301/0.637	0.347/0.184
0.591	0.169	0.270	0.480
0.568	0.167	0.263/0.699	0.528/0.217
0.405	0.221	0.262	0.503
0.319/0.621	0.319/0.172	0.260/0.721	0.619/0.233

entries refer to cloud point determinations. The chromatographic method of analysis used in the determination of the tie-lines was subject to some error. The tie-line data, however, are in good agreement with the binodal curve determined from the cloud-point measurements.

DISCUSSION

Mutual solubility data obtained from a smoothed plot of the experimental data were used to evaluate the two parameters of the van Laar activity coefficient equations for all systems; of the Margules equations for the *n*-hexane, 2-methylpentane, and *n*-octane systems; and of the Scatchard-Hamer equations for the *n*-hexane and 2-methylpentane systems (*6*). The ratios of the van Laar parameters *A* and *B* were in all instances less than 1.5 indicating that the van Laar and Margules equations should be equally applicable to these systems (*10*). The difference between the activity coefficients calculated by the van Laar and Margules equations was negligible for the three systems for which this comparison was made. However, in the dilute homogeneous region, the activity coefficients calculated by the Scatchard-Hamer equations differed considerably from those calculated using the other equations.

Plots of the van Laar parameters, *A* and *B*, for each binary system *vs.* the reciprocal of the absolute temperature gave a linear relation up to within a few degrees of the critical solution temperature. Extrapolation of this linear relation may be a useful method for obtaining values of the parameters from which vapor-liquid equilibrium data can be estimated at the temperatures above the critical solution temperature. Vapor-liquid equilibrium measurements are presently being carried for several of these binary and ternary systems to obtain activity coefficient data in the homogeneous region above and below the critical solution temperature. The data will be used to test the applicability of the two-parameter models and the usefulness of the linear extrapolation.

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Solubilities of Anhydrous Ionic Substances in Absolute Methanol

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THE PURPOSE of the experimentation was to determine the effect of ionic size on the solubility of an ionic compound in methanol. Another object of the investigation was to correlate the solubilities in methanol with those in water, as given in the various handbooks of chemistry.

Data in the literature show large discrepancies for solubilities of inorganic substances in methanol (*1–6*). These discrepancies may be attributed to a small amount of water in methanol and to impurities in the solutes.

EXPERIMENTAL

Chemicals. Anhydrous salts of the alkali and alkaline earth metals in combination with the halides, the nitrate,