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Densities and Molar Volumes of Binary Solutions of Nitroparaffins in Carbon Tetrachloride

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The densities of binary solutions of nitromethane in carbon tetrachloride and nitroethane in carbon tetrachloride were measured at 30°, 35°, and 45° C. The molar volumes and excess molar volumes of mixing were calculated from the observed densities. The data indicated that a single specie of nitroparaffin exists in such binary solutions.

IN RECENT years (*4*), suggestions have been made that nitromethane is a dimer and that solutions of nitromethane in carbon tetrachloride contain equilibrium mixtures of monomer and dimer. The purpose of this investigation was to ascertain whether solutions of either nitromethane or nitroethane in carbon tetrachloride appear to be regular or whether they exhibit wide deviations from regularity. The method used was the determination of density (or a function of density) as a function of concentration. Also, temperature effects were investigated.

EXPERIMENTAL

Specific gravities were taken in a 25-ml. Gay-Lussac pycnometer, Type B bottle (Scientific Glass Apparatus Co., Inc.), using the method described by Weissberger (*12*) and refined by Van Lente (*11*). Weighings (a minimum of three) were made with Christian Becker, Class S, uncalibrated weights. Fisher certified grades of carbon tetrachloride and nitromethane, high purity research samples of nitromethane and nitroethane (Commercial Solvents), and highest purity nitroethane (Brothers Chemical Co.) were used without further purification. No attempt was made to exclude air from the reference liquid (distilled water). The solutions were prepared by mixing volumes of pure components. The estimated cumulative transfer error was ±0.005 mole fraction. Temperatures were regulated (±0.02° C.) by a Precision Scientific Co. bath (No. 66580) and Merc to Merc Model PS-62510-D1 thermoregulator. Temperature readings, precise to ±0.01° C., were obtained with a thermometer calibrated with a National Bureau of Standards thermometer. The precision in the weight readings dictated rounding of the temperature readings (by 0.1° C. or less) to integral values. All calculations were performed on an IBM 1620 computer with 40K storage using an IBM PR 025 monitor with programs written in Fortran II.

RESULTS

Two independent sets of measurements were made at the lowest temperature in order to determine the effect of personal error. This error proved to be of the same order of magnitude as the errors in individual precision. Consequently, only one set of measurements was made at other temperatures. Readings were either corrected to vacuo or discarded if their deviations obeyed a standard discard criterion (*7*). In the case of a suspect result, the final density value was obtained as a weighted average of independent measurements. The final results are given in Table I.

Individual probable errors (*3*) and, where necessary, weighted probable errors were determined for each density. Insomuch as the probable error only indicates wherein 50% of the readings may lie, an average error based upon weight readings appeared to be more indicative of the precision within the individual experiment. An average error was derived from the definition of the specific gravity, d_t^t,

$$d_t^t = \frac{A \pm a}{B \pm b} \tag{1}$$

where A and B are two weight readings with errors a and b, respectively. After expansion of the denominator, a subsequent multiplication yields the series equation

$$d_t^t = \frac{A}{B} \pm \frac{a}{B} \mp \frac{Ab}{B^2} - \frac{ab}{B^2} + \ldots \tag{2}$$

Since the error terms containing $1/B^2$ are of second order compared with the error term containing $1/B$, the average error was taken to be a/B and is given in Table I. With two exceptions, the maximum average error was 0.0002

Table I. Densities and Molar Volumes of Carbon Tetrachloride–Nitroparaffin Solutions

Mole Fraction, RNO_2	30° C. d, g./ml.	30° C. Error × 10^4, g./ml.	30° C. V_M, ml./mole	35° C. d, g./ml.	35° C. Error × 10^4, g./ml.	35° C. V_M, ml./mole	45° C. d, g./ml.	45° C. Error × 10^4, g./ml.	45° C. V_M, ml./mole
				Nitroethane					
0.0	1.5749	1	97.6729	1.5662	0	98.2124	1.5456	1	99.5239
0.1	1.5333	1	95.1878	1.5242	1	95.7523	1.5034	1	97.0816
0.2	1.4897	2	92.6857	1.4818	1	93.1817	1.4614	5	94.4819
0.3	1.4437	1	90.1838	1.4368	1	90.6156	1.4177	2	91.8358
0.4	1.3957	1	87.6425	1.3984	1	87.4702	1.3706	1	89.2450
0.5	1.3447	0	85.1060	1.3485	1	84.8712	1.3207	1	86.6577
0.6	1.2912	1	82.5361	1.2836	1	83.0235	1.2680	2	84.0476
0.7	1.2328	2	80.0577	1.2262	1	80.4912	1.2122	1	81.4209
0.8	1.1707	0	77.5764	1.1650	2	77.9767	1.1515	3	78.8679
0.9	1.1044	1	75.1052	1.1008	2	75.3488	1.0870	2	76.3040
1.0	1.0346	2	72.5551	1.0290	1	72.9542	1.0169	1	73.8186
				Nitromethane					
0.0	1.5749	1	97.6729	1.5662	0	98.2124	1.5456	1	99.5239
0.1	1.5471	2	93.4284	1.5392	1	93.9060	...	.	...
0.2	1.5170	1	89.1648	1.5086	0	89.6655	...	.	...
0.3	1.4842	1	84.8847	1.4751	1	85.4095	1.4553	1	86.5697
0.4	1.4465	1	80.6856	1.4379	0	81.1676	...	.	...
0.5	1.4086	1	76.2712	1.3990	1	76.7941	...	.	...
0.6	1.3630	2	72.0145	1.3557	1	72.4017	...	.	...
0.7	1.3128	1	67.6986	1.3052	1	68.0933	...	.	...
0.8	1.2564	2	63.3513	1.2494	1	63.7103	...	.	...
0.9	1.1917	1	59.0062	1.1854	2	59.3202	...	.	...
1.0	1.1172	0	54.6376	1.1112	1	54.9346	1.0977	0	55.6082

gram per ml. By contrast the maximum probable error was 0.00007 gram per ml.

Finally, Table I shows the molar volumes, V_M, calculated from the observed density values and the assumption that the molecular weight of the solution is an additive function of the molecular weights of the components.

For each binary solution, an excess molar volume of mixing, V^E, has been calculated—viz.,

$$V^E = V_M - x_1(V_M)_1 - x_2(V_M)_2 \qquad (3)$$

where V_M is the molar volume of solution, x_1 and x_2 are the mole fractions of carbon tetrachloride and nitroparaffin, respectively, and $(V_M)_1$ and $(V_M)_2$ are the molar volumes of carbon tetrachloride and nitroparaffin, respectively. The results are given in Table II.

Table III summarizes pertinent literature values.

DISCUSSION

In this pycnometer method, precision is dependent, in part, upon the formation of a stable surface on the capillary tip. The errors in Table I show that a more stable surface was obtained with nitromethane than with nitroethane. This difficulty is contrary to that which is expected from a comparison of the volatilities of the two compounds. A possible explanation is that the surface tension of nitroethane is less than that of nitromethane (*5*). Particular difficulty was encountered in the determinations involving those solutions for which the mole fraction of nitroparaffin was 0.4 and 0.5. This was true for both compounds at all temperatures.

Plots of density as a function of mole fraction of nitroparaffin and density as a function of weight fraction of nitroparaffin were curvilinear. Plots of density as a function of volume fraction of nitroparaffin and molar volume as a function of mole fraction of nitroparaffin were linear. The close adherence to linearity of these latter plots must be interpreted as meaning that any deviation from ideality is slight. If there is an equilibrium between different species of nitroparaffin molecules, one specie must predominate.

Table II. Calculated Volume of Mixing for Nitroparaffin Binary Solutions

Mole Fraction, RNO_2	V^E, 30° C., Ml./Mole	V^E, 35° C., Ml./Mole	V^E, 45° C., Ml./Mole
	Nitroethane		
0.0	0.0000	0.0000	0.0000
0.1	0.0266	0.0658	0.1283
0.2	0.0364	0.0210	0.0990
0.3	0.0462	−0.0193	0.0235
0.4	0.0168	−0.6389	0.0032
0.5	−0.0080	−0.7121	−0.0135
0.6	−0.0661	−0.0339	−0.0531
0.7	−0.0328	−0.0404	−0.1094
0.8	−0.0022	−0.0491	−0.0918
0.9	−0.0384	−0.1312	−0.0852
1.0	0.0000	0.0000	0.0000
	Nitromethane		
0.0	0.0000	0.0000	0.0000
0.1	0.0590	0.0215	...
0.2	0.0990	0.1087	...
0.3	0.1223	0.1804	0.2205
0.4	0.2268	0.2664	...
0.5	0.1160	0.2206	...
0.6	0.1628	0.1560	...
0.7	0.1504	0.1754	...
0.8	0.1066	0.1201	...
0.9	0.0650	0.0579	...
1.0	0.0000	0.0000	0.0000

Scatchard (*6*) has reported that the excess volume of mixing can be fitted to a series of the form

$$V^E = a_0x_1x_2 + a_1x_1x_2(x_1 - x_2) + \ldots \qquad (4)$$

where the a_i are constants. The V^E values of nitromethane, in Table II, show the parabolic nature indicated by the leading term of Equation 4. However, the corresponding nitroethane values have the cubic form which results if the leading term of Equation 4 vanishes. The simplest explanation for these facts is that the deviations from ideality, in the case of nitroethane, are second order whereas they are first order for nitromethane. This explanation is substantiated by the magnitude of the V^E values given in Table II. Thacker and Rowlinson (*8*) have suggested that the absence of a quadratic term may imply that the configuration energy cannot be written as the sum of two-body interactions.

Table III. Summary of Literature Values

Temp., °C.	Density of Carbon Tetrachloride, G./Ml.	Density of Nitromethane, G./Ml.	Density of Nitroethane, G./Ml.
30	1.57478 (*14*)	1.12439 (*10*)	1.03870 (*10*)
	1.57480 (*13*)	1.12453 (*13*)	
35	1.56480 (*2*)	1.11700 (*2*)	
	1.56478 (*9*)		
45	1.5442 (*2*)	1.1033 (*2*)	

Brown and Smith (*1*) have reported the maximum value of V^E for nitromethane–carbon tetrachloride solutions at 25°C. to be 0.17 ml. per mole. The present results are in agreement with this value as well as with the graphical results presented by Brown and Smith (*2*) and with their conclusion that the volume of mixing of solutions of which carbon tetrachloride is one component increases with an increase in temperature.

CONCLUSIONS

The density and volume data of binary solutions (in carbon tetrachloride) of nitroparaffins in the temperature range of 30° to 45°C. indicate that the solutions are nearly ideal. Nitroethane forms a more ideal solution than nitromethane. The conclusion follows that the nitroparaffin molecule in these solutions exists, predominantly, as a single specie. This conclusion applies whether one considers acid dissociation or dimer dissociation. In both instances, the more polar nature of nitromethane would predict a greater perchance for dissociation.

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Thermodynamic Properties of 1,1,1,2,2-Pentafluoropropane (Refrigerant 245)

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Experimental volumetric and spectral data have been used to calculate the thermodynamic properties of 1,1,1,2,2-pentafluoropropane. Properties are presented for the saturated liquid and vapor from −40° F. to the critical temperature, 224.52° F. The data for the superheated vapor range from the saturation temperature to 700° F. The properties listed are volume, enthalpy, entropy, heat capacity at constant pressure, and heat capacity ratio as functions of temperature and pressure.

IN DESIGNING refrigeration equipment using a particular refrigerant, tables of thermodynamic properties of the refrigerant and graphs representing the properties are a virtual necessity. This paper is part of a continuing program in progress at the UCON Refrigerant Laboratories, Union Carbide Corp., to compile tables and construct graphs presenting the thermodynamic properties of halogenated hydrocarbons.

The present study provided detailed information on the thermodynamic properties of Refrigerant 245. The properties listed are volume, enthalpy, and entropy as functions of temperature and pressure. The values of the thermodynamic properties were computed from analytical expressions representing the heat capacity of the ideal vapor and the pressure-volume-temperature (*P-V-T*) relations of the refrigerant.

The ideal vapor heat capacity was calculated by Angell (*1*) from the fundamental frequencies of vibration of the molecule and assumed molecular dimensions and conformation, using standard methods of statistical mechanics. The