Viscosities of Binary Solutions of Nitroparaffins in Carbon Tetrachloride

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The viscosities of binary solutions of nitromethane and nitroethane in carbon tetrachloride were determined at 30°, 35°, and 45°C. The excess free energies of mixing were calculated from the observed viscosities. In these binary solutions, the two nitroparaffins differed with respect to the factors responsible for deviations from ideality (in the viscosity sense). The deviations are within the limits of empirical mixture laws.

THIS INVESTIGATION is a continuation of the effort to determine, by a study of physical properties, if solutions of nitromethane or nitroethane in carbon tetrachloride are regular (6). This paper discusses the viscosity (or a function of viscosity) and free energy of mixing as functions of concentration, and their relation to the molecular structure of the pure nitroparaffins. In addition, two of the many empirical relations among the component viscosities of binary solutions are examined in order to acquire a proper perspective between older and more modern investigations dealing with regularity.

EXPERIMENTAL

Flow time was measured in a Cannon-Fenske viscometer with a Minerva stopwatch (precision ±0.2 second), following the method described by Weissberger (16) and refined by Van Lente (15). A minimum of five time readings were taken in each of two different viscometers. The flow times for water varied from 54.4 to 42.3 seconds and from 46.9 to 36.1 seconds, respectively.

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. The solutions were prepared by mixing volumes of pure components. The estimated cumulative transfer error was ±0.005 mole fraction. The solution densities of Gunter et al. (6) were used, except for certain nitromethane solutions at 45°C. whose densities were estimated from measured densities at 30° and 35°C.

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

Table I summarizes the average viscosity values, η, after individual time readings have been subjected to a standard discard criterion (18). It also gives the average deviation

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of the viscosity values for each viscometer. In calculating the η values in Table I, water viscosity values given by Dorsey (1) and carbon tetrachloride viscosity values (the underlined values in Table I) calculated from the temperature equation given by Weissberger et al. (17) were used. Calculated fluidity values, ϕ, are also given in Table I.

Table I shows each average deviation from the mean viscosity value calculated from the two values obtained with the individual viscometers. With only six exceptions, the probable error of each average viscosity at a given temperature was the same. These probable errors (10^4 cp.) were 8, 16, and 9 for 30°, 35°, and 45°C., respectively. The exceptional cases had probable errors one unit greater.

The average deviation and the average probable error for each set of time readings were 0.06 and 0.02 second, respectively, the extreme values being 0.00 and 0.28 second and 0.00 and 0.07 second, respectively. The error pattern was random with respect to solution mole fraction, temperature, and measuring viscometer. Measurements were made at 30°C. with each grade of CCl_4 and of $C_2H_5NO_2$. Measurements were made at 30° and 35°C. on a 0.3 mole fraction solution of CH_3NO_2, to ascertain if there were any changes in viscosity with time (1- to 2-month intervals). No viscosity effects with respect to chemical grade or time of preparation could be detected within the limits of the determined probable errors.

The results for pure CH_3NO_2 are in close agreement with the values predicted by the Friend and Hargreaves equation (3); similar comparisons for $C_2H_5NO_2$ show the measured results to be 7 to 9% low. Since Wright, Murray-Rust, and Hartley (19) have shown that a slight amount of water lowers the viscosity of CH_3NO_2, there is the possibility of water contamination. However, in the one direct comparison to a measurement on a compound of the same purity at the same temperature as the present measurements, the current value agrees with the literature and both values are 2.5% below the predicted Friend and Hargreaves value. Literature values are tabulated in Table II.

The excess free energy of mixing for each solution at each temperature, ΔG_m^t, was calculated from

$$\ln \eta_s V_M = x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2 + \frac{\Delta G_m^t}{RT} \qquad (1)$$

where x_i are the mole fractions, η_i are the viscosities of the components, η_s is the viscosity of the solution, V_i are the molal volumes of the components, V_M is the molal volume of the solution, and subscripts 1 and 2 refer to carbon tetrachloride and nitroparaffin, respectively. The results are presented in Table III.

Table I. Viscosities and Fluidities of Carbon Tetrachloride–Nitroparaffin Solutions

Mole Fraction RNO_2	30° C.			35° C.			45° C.		
	η, cp.	Av. deviation, cp. × 10⁴	ϕ, cp.⁻¹	η, cp.	Av. deviation, cp. × 10⁴	ϕ, cp.⁻¹	η, cp.	Av. deviation, cp. × 10⁴	ϕ, cp.⁻¹
				NITROETHANE					
0.0	0.842	...	1.188	0.786	...	1.272	0.691	...	1.447
0.1	0.7718	113	1.2959	0.7423	139	1.3476	0.6487	24	1.5415
0.2	0.7427	33	1.3464	0.6974	6	1.4339	0.6201	27	1.6127
0.3	0.7058	17	1.4173	0.6680	26	1.4969	0.5962	27	1.6772
0.4	0.6831	20	1.4640	0.6479	10	1.5434	0.5782	16	1.7294
0.5	0.6569	5	1.5222	0.6260	15	1.5973	0.5609	34	1.7829
0.6	0.6415	8	1.5588	0.6063	20	1.6494	0.5460	31	1.8315
0.7	0.6240	5	1.6026	0.5927	18	1.6871	0.5328	34	1.8770
0.8	0.6126	6	1.6323	0.5834	24	1.7140	0.5246	26	1.9061
0.9	0.6123	7	1.6332	0.5735	11	1.7436	0.5207	13	1.9206
1.0	0.6062	19	1.6496	0.5717	12	1.7490	0.5208	1	1.9199
				NITROMETHANE					
0.0	0.842	...	1.188	0.786	...	1.272	0.691	...	1.447
0.1	0.7767	7	1.2874	0.7408	56	1.3500	0.6485[a]	13	1.5419
0.2	0.7448	25	1.3426	0.6988	35	1.4311	0.6213[a]	24	1.6095
0.3	0.7173	9	1.3940	0.6673	20	1.4985	0.5970	33	1.6752
0.4	0.6971	29	1.4345	0.6509	12	1.5364	0.5764[a]	27	1.7349
0.5	0.6667	6	1.4999	0.6305	7	1.5861	0.5533[a]	25	1.8072
0.6	0.6402	19	1.5621	0.6024	20	1.6599	0.5327[a]	14	1.8771
0.7	0.6152	35	1.6255	0.5769	16	1.7333	0.5140[a]	25	1.9457
0.8	0.5924	9	1.6880	0.5634	11	1.7750	0.4996[a]	18	2.0015
0.9	0.5824	1	1.7169	0.5522	14	1.8108	0.4945[a]	20	2.0222
1.0	0.5737	51	1.7431	0.5507	13	1.8157	0.5009	16	1.9962

[a] Calculated with extrapolated density values.

Table II. Summary of Literature Values

Temp., °C.	Viscosity, Cp.	
	Nitromethane	Nitroethane
30	0.5873[a] (3)	0.6683[a] (3)
	0.595 (14)	
	0.574 (13)	
35	0.5564[a] (3)	0.6300[a] (3)
45	0.5018[a] (3)	0.5630[a] (3)

[a] Calculated from derived temperature equation.

The values of the rheochor (2) and Souders' constant (12) have been calculated directly from the measured viscosities and average molecular weights and also assuming that these quantities are additive with respect to mole fraction. The calculated values are compared (Table IV) to the values obtained from the summation of appropriate atomic factors, assuming additivity with respect to mole fractions. The two methods of calculation from experimental data agree within 2%; the values for CCl_4 calculated from atomic factors are within 4%. The Souders' constants calculated from atomic factors for CH_3NO_2 and $C_2H_5NO_2$ are 5 and 10% low, respectively; the rheochor values are within 1%. The abnormal CCl_4 rheochor and Souders' constant values have been noted previously (2, 12) and attributed to the accumulation of negative groups. In all cases, the agreement between the values calculated from experimental data and the values from atomic factors warrants an extension, for these binary solutions, of the conclusions by Reid and Sherwood (11) that Souders' method can be used to estimate viscosities empirically. For these solutions, the rheochor could be used in a like manner.

DISCUSSION

Isotherms of viscosity vs. volume per cent (10) indicate a moderate positive deviation in the activity coefficients. These isotherms exhibit a small minimum in the region of 0.9 volume % nitroparaffin. Since the minima are of the same magnitude as the average deviation in the viscosity, they may result from experimental error in a region of zero slope. Isotherms of fluidity vs. mole fraction were nonlinear, indicating a deviation from the simplest description of ideal mixtures (5).

The more negative values of ΔG_m^t for nitroethane in carbon tetrachloride would indicate that those solutions are more nonideal in the viscosity sense. However, plots of $\Delta G_m^t / RT$ vs. V^E indicate that the nonideal behavior in nitroethane solutions is primarily associated with expansion upon mixing, but the entropy of mixing makes a substantial contribution to the nonideal behavior of nitromethane solutions. Reed and Taylor (10) place solutions with these differences in free energy properties in different subclasses.

The empirical techniques—e.g., rheochor and Souders' constant—are not as sensitive a means of detecting interaction as the free energy of mixing. Although many studies have shown that the rheochor changes with temperature for associated substances (2, 4, 9), these same studies have considered the values for CH_3NO_2 and CCl_4 to be temperature-independent. The results in Table IV show no significant temperature dependence for any pure component or mixture rheochor value, thus verifying the assertion that this technique is rather insensitive to the moderate amount of irregularity indicated by Table III. Musulin (8) has shown that no quantitative estimate of possible association constants can be derived from the differences between the observed and calculated values of the additive-constitutive properties given in Table IV.

The limited number of temperature data points precluded any attempt to test the applicability of modern significant structure or free volume theories (7) to liquid mixtures.

CONCLUSIONS

Reed and Taylor (10) have suggested that if ΔG_m^t has a smaller negative value than expected from the volume

Table III. Excess Free Energy of Mixing for Nitroparaffin–Carbon Tetrachloride Solutions

Mole Fraction RNO$_2$	Nitromethane			Nitroethane		
	$-\Delta G_m^{30}$, cal.-mole^{-1}	$-\Delta G_m^{35}$, cal.-mole^{-1}	$-\Delta G_m^{45}$, cal.-mole^{-1}	$-\Delta G_m^{30}$, cal.-mole^{-1}	$-\Delta G_m^{35}$, cal.-mole^{-1}	$-\Delta G_m^{45}$, cal.-mole^{-1}
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	17.3	6.4	11.6	30.3	12.9	18.9
0.2	12.6	13.0	10.9	31.8	30.0	27.8
0.3	6.8	13.7	9.2	41.3	35.8	33.8
0.4	-3.6	2.8	5.7	40.5	38.4	34.5
0.5	-0.9	-1.1	7.4	44.0	40.3	35.6
0.6	0.1	5.4	9.4	39.0	35.7	35.2
0.7	3.2	12.1	12.9	36.4	30.8	34.0
0.8	7.8	10.1	15.4	28.7	22.4	27.1
0.9	2.7	8.7	11.5	10.9	16.0	16.0
1.0	0.0	0.0	0.0	0.0	0.0	0.0

Table IV. Rheochor and Souders' Constant for Nitroparaffin–Carbon Tetrachloride Solutions

Mole Fraction RNO$_2$	Calculated from Solution Viscosity			Calculated from Component Viscosities			Lit. Value[a]
	30° C.	35° C.	45° C.	30° C.	35° C.	45° C.	
			NITROETHANE[b]				
0.0	127.5	127.1	126.7	127.5	127.1	126.7	122.0
0.1	122.9	123.0	122.6	123.8	123.4	123.1	119.0
0.2	119.1	118.8	119.5	120.2	119.8	119.5	115.9
0.3	115.1	114.9	114.8	116.5	116.2	115.9	112.9
0.4	111.4	110.5	111.1	112.8	112.5	112.3	109.8
0.5	107.8	106.7	107.5	109.2	108.9	108.7	106.8
0.6	104.1	104.0	103.9	105.5	105.3	105.1	103.8
0.7	100.6	100.5	100.4	101.9	101.6	101.5	100.7
0.8	97.3	97.2	97.0	98.2	98.0	97.9	97.9
0.9	94.2	93.7	93.8	94.5	94.4	94.3	94.6
1.0	90.9	90.7	90.7	90.9	90.7	90.7	91.6
			NITROMETHANE[b]				
0.0	127.5	127.1	126.7	127.5	127.1	126.7	122.0
0.1	120.7	120.6	120.2	121.5	121.2	120.9	116.6
0.2	114.6	114.3	114.1	115.6	115.3	115.0	111.1
0.3	108.6	108.3	108.2	109.6	109.4	109.1	105.8
0.4	102.8	102.6	102.5	103.7	103.4	103.2	100.3
0.5	96.7	96.7	96.8	97.7	97.5	97.4	94.9
0.6	90.8	90.6	91.2	91.8	91.6	91.5	89.5
0.7	85.0	84.8	85.5	85.8	85.7	85.6	84.0
0.8	79.1	79.1	79.7	79.9	79.8	79.8	78.7
0.9	73.5	73.4	73.9	73.9	73.9	73.9	73.2
1.0	68.0	68.0	68.0	68.0	68.0	68.0	67.8
			NITROETHANE[c]				
0.0	280.0	280.1	281.1	280.0	280.1	281.1	290.2
0.1	271.1	271.9	272.8	272.2	272.4	273.3	280.6
0.2	263.2	263.3	264.4	264.5	264.6	265.5	270.9
0.3	255.1	255.2	256.2	256.8	256.9	257.8	261.3
0.4	247.3	245.7	248.3	249.0	249.2	250.0	251.7
0.5	239.4	237.7	240.4	241.3	241.4	242.2	242.0
0.6	231.7	231.9	232.6	233.6	233.7	234.5	232.4
0.7	224.2	224.4	224.8	225.9	226.0	226.7	222.8
0.8	216.9	217.0	217.5	218.1	218.2	218.9	213.2
0.9	210.0	209.5	210.2	210.4	210.5	211.2	203.5
1.0	202.7	202.8	203.4	202.7	202.8	203.4	193.9
			NITROMETHANE[c]				
0.0	280.0	280.1	281.1	280.0	280.1	281.1	290.2
0.1	266.2	266.6	267.2	267.1	267.3	268.2	275.0
0.2	253.3	253.4	254.2	254.3	254.5	255.4	259.8
0.3	240.4	240.5	241.5	241.5	241.7	242.5	244.6
0.4	228.0	228.8	229.1	228.8	228.9	229.7	229.4
0.5	214.8	215.2	216.6	215.9	216.1	216.8	214.2
0.6	202.1	202.1	204.2	203.1	203.3	204.0	199.1
0.7	189.4	189.4	191.6	190.3	190.5	191.2	183.9
0.8	176.6	176.8	178.9	177.5	177.7	178.3	168.7
0.9	164.3	164.3	166.0	164.7	164.9	165.5	153.5
1.0	151.9	152.2	152.6	151.9	152.2	152.6	138.3

[a] Calculated from atomic values (2, 3, 12). [b] Rheochor. [c] Souders' constant.

expansion upon mixing, the molecular group which is displaced contains molecules in some association. This is consistent with the fact that the more polar nitromethane is more likely to dimerize than nitroethane. The moderate amount of nonideality is consistent with the conclusion based on density data (6) that these binary solutions are nearly ideal.

ACKNOWLEDGMENT

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P-V-T-X Properties of Associated Vapors of

Formic and Acetic Acids

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The P-V-T-X properties of the associated vapors of acetic and formic acids and their mixtures were measured over the range of 50° to 125°C. and 30 to 700 mm. of Hg. The presence of clusters of more than two molecules is strongly suggested in the pure acids and mixtures. The data were interpreted in terms of an ideal gas association theory. Dimerization constants and heat of association are presented for the pure and crossdimer formations.

CARBOXYLIC ACID VAPORS have long been known to deviate appreciably from ideal gas behavior (6, 18), the indications being that the prime contribution to nonideality is the formation of low-order molecular clusters. Several investigations (2, 5, 8, 9, 11) have shown that intermolecular hydrogen bonding is responsible for the formation of relatively stable clusters of molecules which thus cause a trend in the apparent molecular weight as a function of both temperature and pressure.

This work was an experimental study of the volumetric properties of the mixtures of the first two members of the carboxylic acid homologous series. Comprehensive experimental data for the pure acids were available in the literature (1, 2, 3, 5, 6, 7, 11, 12, 15, 16, 18, 21); however, data for the mixtures of these acids appear to be lacking. As a check on the reliability of the apparatus used by the authors, pure component P-V-T data were also measured and compared with data from the literature.

EXPERIMENTAL

Materials. Formic acid was supplied by the British Drug Houses, Poole, England, as 98% minimum formic acid, the balance being less than 0.01% impurities other than water. This acid was purified by a method suggested by Winstein and Marshall (23). The refractive index of the purified acid, 1.3710, compares favorably with values of 1.3710 (1) and 1.3714 (10), all at 20°C. The density of the acid at 20°C. was 1.2209, which compares with 1.2206 (3) and 1.2201 (8). These data indicate a purity of at least 99.9% formic acid. Formic acid is readily decomposed at high temperatures; however, in the temperature range of this investigation data from the literature (1, 3, 13) indicate that this should produce a negligible effect.

Acetic acid was supplied by the J. T. Baker Chemical Co., Phillipsburg, N. J., with a guranteed purity of 99.9%. Further tests of purity performed in this laboratory confirmed this figure. The index of refraction was 1.3720,