SURFACE TENSIONS OF BINARY SOLUTIONS OF NITROPARAFFINS IN CARBON TETRACHLORIDE

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ABSTRACT. — The surface tensions of binary solutions of nitromethane in carbon tetrachloride and nitroethane in carbon tetrachloride were determined by the ring method at 30°, 35°, and 45°C. Assuming perfect solutions, the surface excesses and the surface entropies and enthalpies were calculated. The surface entropies indicated increasing ordering in the solutions. Surface entropies and enthalpies of mixing were also calculated. These calculations indicated that nitroethane formed a more ideal solution than nitromethane. Nitromethane showed evidence of association as well as disassociation. The deviations for these solutions are within the limits of an empirical mixture law.

This investigation is a continuation of the series of simple physical measurements upon binary solutions of nitroparaffins in carbon tetrachloride. The immediate purpose of such measurements is to place into the literature accurate solution data concerning commercial chemicals that have important applications in automotive fuels. Although data involving pure nitroparaffins, particularly nitromethane is plentiful, solution data is sparse (cf. Timmermans (1959)). The current series of papers indicates the degree to which solution values, for engineering purposes, can be obtained by interpolation and/or extrapolation of existing data and by prediction from empirical formulae.

A second major objective of the current investigations is to obtain inferential information concerning the structure of these binary solutions. First, are the solutions ideal, regular, or irregular? Second, if the solutions are irregular, what is the nature of the irregularity? Gunter *et al.* (1967) by means of density measurements have shown that these binary solutions are irregular with respect to volume effects. Wettaw *et al.* (1969) by means of viscosity measurements have shown that these binary solutions are irregular with respect to entropy effects. The present paper shows the nature of irregularities determined by surface tension measurements. Since inferences concerning the bulk solution may differ from inferences concerning the surface layer, this work has the advantage of providing two sets of conclusions with one set of measurements. Third, how do solutions of homologous members of the nitroparaffin series differ? The previous sets of measurements indicated that the first member of the series is quite different from the second member. Whether or not the same conclusion is true for each different physical property is determined only by making the measurement.

This paper discusses the surface tension, the surface excess, the surface entropy and enthalpy, and the excess surface entropy and enthalpy

of mixing as functions of concentrations, and their relation to the molecular structure of the pure nitroparaffins. In order to acquire a proper perspective between older and more modern investigations of regularity, one empirical relationship, the parachor, is examined.

Experimental

Fisher certified and spectro grades of carbon tetrachloride, Fisher certified grade 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 solutions, in closed, ground glass containers, were brought to equilibrium in a Precision Scientific Co. bath (No. 66580) and regulated ($\pm 0.02^{\circ}$C.) with a Merc to Merc Model PS-62510-D1 thermoregulator. Temperature readings, precise to $\pm 0.01^{\circ}$C., were obtained with a thermometer calibrated with a National Bureau of Standards thermometer. The precision in the preparation of solutions dictated rounding of the temperature readings by 0.1°C. or less to integral values.

The apparent surface tensions were obtained, after rapid transfer of the solutions from the bath, by the ring method using a Fisher Surface Tensiometer, Model 20. True surface tensions were calculated with the formula for the correction factor,

$$\gamma = .7250 + \sqrt{\left[\frac{.04534 - 1.679}{(R_{wire}/R_{ring})}\right] + \left[\frac{.01452\ D_{Av}}{C^2\ (D_{liq} - D_{vap})}\right]} \quad (1)$$

where D_{Av} is the average dial reading; γ is the true surface tension; R_{wire} and R_{ring} are the radii of the suspending wire and the platinum ring, respectively; C is the circumference of the ring; and D_{liq} and D_{vap} are the densities of the solution and the vapor in equilibrium with the solution, respectively. Vapor densities were estimated, by linear interpolation, for use in the correction calculation; liquid densities were taken directly from or estimated from Gunter *et al.* (1967).

Results

The number of readings and the average deviation of each set of readings are given in Table 1. These averages sometimes represent readings taken on different days; sometimes they represent readings taken on different sample grades; and sometimes they represent readings on repetitive trials taken to ascertain temperature loss in the transfer process. There is no explanation for the readings with the greatest deviation, i.e. 0.8 and 0.9 $CH_3\ NO_2$, except lack of experimental technique. Nevertheless, even these readings are acceptable for an instrument whose scale gradations are given in 0.1 units. Each set of readings was processed by a computer program which calculated the average deviation and the probable error of an individual reading, tested each individual reading for discard as being beyond normal experimental error, and, if necessary, recalculated the averages and the deviations. The discard judgment was based on Chauvenet's criterion (Worthing and Geffner [1943]). Insomuch as

TABLE 1.—Surface Tensions of Carbon Tetrachloride-Nitroparaffin Solutions.

Mole Fraction (RNO_2)	30°C				35°C				45°C			
	γ (dyne/cm)	Probable Error (dyne/cm)	No. Read.	Av. Dev. Dial Read.	γ (dyne/cm)	Probable Error (dyne/cm)	No. Read.	Av. Dev. Dial Read.	γ (dyne/cm)	Probable Error (dyne/cm)	No. Read.	Av. Dev. Dial Read.
Nitromethane												
0.0	26.70	.01	40	.08	25.77	.01	26	.04	24.65	.01	26	.09
0.1	26.88	.00	10	.08	25.90	.00	10	.00	24.77	.01	19	.10
0.2	27.08	.02	10	.07	26.01	.01	15	.04	24.95	.01	14	.04
0.3	27.13	.02	15	.11	26.29	.00	15	.04	25.22	.01	13	.03
0.4	27.35	.01	30	.09	26.42	.02	15	.08	25.36	.02	15	.10
0.5	27.51	.01	20	.03	26.50	.01	20	.10	25.81	.01	12	.04
0.6	27.72	.00	20	.01	27.08	.01	15	.05	26.15	.01	12	.05
0.7	28.37	.01	20	.08	27.79	.01	15	.07	26.76	.01	12	.05
0.8	29.70	.02	20	.08	29.34	.03	40	.21	27.96	.01	12	.06
0.9	31.76	.01	15	.09	31.46	.04	20	.22	29.84	.01	12	.05
1.0	35.44	.01	15	.03	34.00	.01	12	.07	32.74	.02	9	.07
Nitroethane												
0.0	26.70	.01	40	.08	25.77	.01	26	.04	24.65	.01	26	.09
0.1	26.62	.00	35	.05	25.87	.01	25	.09	24.79	.01	9	.06
0.2	26.73	.00	20	.02	26.08	.01	15	.06	24.89	.02	9	.06
0.3	27.11	.01	10	.03	26.40	.01	25	.09	25.17	.01	9	.04
0.4	27.23	.01	10	.03	26.56	.01	15	.07	25.50	.02	9	.08
0.5	27.55	.00	10	.02	26.84	.01	15	.06	25.83	.02	9	.07
0.6	27.96	.00	10	.00	27.42	.00	15	.04	26.19	.02	9	.09
0.7	28.59	.01	5	.02	28.01	.02	5	.08	26.72	.02	9	.06
0.8	29.24	.01	5	.02	28.62	.00	10	.00	27.41	.01	9	.04
0.9	29.86	.02	5	.06	29.39	.01	5	.04	28.22	.01	9	.05
1.0	30.66	.01	20	.05	30.16	.02	5	.04	29.11	.02	9	.08

this particular criterion was used for decision making, the standard deviation of each set of readings was not recovered in the computer output. The standard deviation, ascertained by trial calculations, is approximately 1.1 to 1.2 the average deviations tabulated in Table 1.

The probable error of the true surface tension calculated with Equation (1) was calculated in the usual formulas for propagation of errors (cf. Daniels *et al.* (1962)) using the errors given by Gunter *et al.* (1967) for D_{fs_1}, the average deviations of $D_{\Delta v}$, and zero error in R_{wire}, R_{ring}, C, and D_{vis}. The probable errors are given in Table 1 along with the true surface tensions calculated from Equation (1). The D_{fs_1} determination involved the compounding of errors from several sources which makes it, relatively, less determined than $D_{\Delta v}$ which involved a single, accurate measurement. The probable errors shown in Table 1 reflect the weighted importance of the errors in D_{fs_1}.

Individual measurements at 30°C. showed no significant variation for the different grades of carbon tetrachloride and nitromethane. The results are in good agreement with the nitroparaffin values interpolated from the ring method data of Boyd and Copeland (1942). The results are lower than the data measured by and/or the data calculated from the non-ring methods used by Snead and Clever (1962) and Thompson, Coleman, and Helm (1954). The greatest 30° deviation from the literature involves CCl_4 and is probably due to slight evaporation loss during transfer. On the other hand, the deviation found in $C_2H_5NO_2$ is undoubtedly due to the impurities inherent in the grade of chemical used. Although of superior quality, the $C_2H_5NO_2$ is not of the great purity as the CH_3NO_2 and CCl_4. No literature values were available at 35°C or 45°C. One may surmise that the present data are of quality comparable to that of the 30°C data with somewhat greater experimental error due to evaporation at the higher temperature. A comparison of the rapid ring method with a more accurate technique, e.g. the maximum bubble pressure method, is obtained by comparing the values from the literature found in Table 6. No literature data for the solutions are available but the present data can be construed to be of the same excellent quality as the data for our pure compounds.

The relative surface adsorption (surface excess) of the nitroparaffin (component 2) with respect to the carbon tetrachloride (component 1). $\Gamma_{2,1}$ was calculated from the equation for perfect solutions (Defay *et al.* (1966)),

$$\Gamma_{2,1} = -\frac{x_2}{RT}\left(\frac{\partial \gamma}{\partial_2 x}\right)_{T,P} \qquad (2)$$

where x_2 is the mole fraction of the nitroparaffin, R is the ideal gas constant, T is the absolute temperature, and P is the ambient pressure. The derivative in Equation (2) was obtained analytically from a least squares fit of the surface tension data to a quadratic function of the mole fraction. The choice of a quadratic function was arbitrary but limited by the criteria of a good representation of the input data and statistical reliability for the number of degrees of freedom. The zero degree and first degree polynomials are eliminated by the first criterion while any polynomial of quintic degree or higher is eliminated by the second criterion. Consideration of the errors inherent in determining a derivative through the use of data fit plus the errors in assuming the

validity of Equation (2) suggested that cubic degree or higher polynomials were an over determination. The absolute surface adsorption of the nitroparaffin, Γ_2, was calculated assuming a dividing surface under an inhomogeneous monolayer and a mixture surface tension which is a linear function of the surface adsorption mole fraction, $\Gamma_2/_2 + \tau_1$), (van Rysselberghe (1938)). The results are given in Table 2. In general, the results illustrate the principle that the substance of lower surface tension is concentrated at the surface. For example, the negative values of $\Gamma_{2,1}$ reflect the increasing deficiency of RNO_2 with respect to CCl_4 (the substance of lower surface tension). The values of Γ_2 are consistent with the size of the nitroparaffin molecule. The amount of excess is proportional to the difference in surface tensions of the components of the solution. The more negative values of $\Gamma_{2,1}$ for CH_3NO_2

TABLE 2.—Surface Adsorptions of Carbon Tetrachloride-Nitroparaffin Solutions.

Mole Fraction (RNO_2)	Stated in Units of Q cm^{-2} x 10^{10}					
	$\Gamma_{2,1}$			Γ_2		
	30°C	35°C	45°C	30°C	35°C	45°C
Nitromethane						
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	0.190	0.143	0.107	—0.0462	—0.0241	—0.0154
0.2	0.152	0.0776	0.334	—0.0340	—0.0107	—0.00601
0.3	—0.115	—0.196	—0.220	0.0159	0.0369	0.0470
0.4	—0.610	—0.678	—0.653	0.0836	0.0997	0.110
0.5	—1.33	—1.37	—1.27	0.152	0.149	0.254
0.6	—2.29	—2.27	—2.06	0.221	0.327	0.368
0.7	—3.47	—3.37	—3.03	0.392	0.545	0.537
0.8	—4.88	—4.69	—4.18	0.735	1.11	0.872
0.9	—6.51	—6.21	—5.51	1.18	2.06	1.37
1.0	—8.38	—7.94	—7.03	.....	.....	.....
Nitroethane						
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	—0.0219	—0.0416	—0.0313	—0.00316	0.0113	0.0121
0.2	—0.112	—0.147	—0.128	0.00451	0.0642	0.0379
0.3	—0.271	—0.317	—0.291	0.00989	0.207	0.129
0.4	—0.498	—0.550	—0.519	0.159	0.271	0.283
0.5	—0.794	—0.847	—0.814	0.301	0.405	0.455
0.6	—1.16	—1.21	—1.17	0.521	0.807	0.634
0.7	—1.59	—1.63	—1.60	1.02	1.32	0.947
0.8	—2.09	—2.12	—2.09	1.68	1.82	1.43
0.9	—2.66	—2.67	—2.65	2.08	2.98	2.15
1.0	—3.30	—3.29	—3.27	.....	.....	.....

mirror the greater differential in the γ-values of CH_3NO_2 and CCl_4 as compared to $C_2H_5NO_2$. Although the specific values of T_2 depend upon the mode of calculation (the choice of surface), these qualitative conclusions remain invariant (Guggenheim and Adam (1933)).

The surface entropy per unit area, s_σ, was obtained from a least squares fit of surface tension data to a linear function of temperature. The linear function was chosen because of the well-known behavior of surface tension as a function of temperature (Partington, 1951). This fortuitous functional behavior results in a particularly simple calculation whereby the slope of the least squares fit is simply $(d\gamma/dT)_{P,A}$ (A being the surface area). The identification of this slope as s_σ results from the alternate view of surface tension as surface free energy and the application of the usual thermodynamic equations to the surface layer. The heat of extension of the surface per unit area (latent heat per unit area), l_σ, was calculated from s_σ and, then, the enthalpy of extension of the surface per unit area, h_σ, was calculated from l_σ and γ. That is, the latent heat is obtained by a temperature multiplication of the slope of the least squares linear plot. The enthalpy then follows immediately from the first law of thermodynamics, that is, from the conservation of energy. The values of s_σ and h_σ are given in Table 3.

The surface entropy per mole, s_m, was calculated from the slope of a Ramsay-Shields (1893) plot determined by the method of least squares. This calculation proceeds exactly as that of the preceding paragraph but the independent variable is not γ but $\gamma(MV)^{2/3}$, where M is the molecular mass of the compound and V is the molar volume of the compound. For solution data, M was obtained by the assumption that mass of the solution is additive with respect to the mole fraction of the components,

$$M = x_1M_1 + x_2M_2 \qquad (3)$$

where x_1 and x_2 are the mole fractions of CCl_4 and nitroparaffin, respectively; M_1 and M_2 are the molecular masses of CCl_4 and nitroparaffin, respectively; and M is the molecular mass of the solution. The molar volumes were taken from Gunter *et al.* (1967). Whereas γ is the surface free energy, the quantity $\gamma(MV)^{2/3}$ is the free molecular surface-energy. As is true for

$$\gamma,\gamma(MV)^{2/3}$$

fits well a linear function of temperature, if the temperature is given in absolute terms. In a manner analogous to the calculation of l_σ and h_σ, the heat of extension of the surface per mole (latent heat per mole), l_m, and the enthalpy of extension of the surface per mole, h_m, were calculated from s_m. The entrophies and enthalpies are tabulated in Table 3.

The values of s_σ and h_σ for pure nitroparaffins are in good agreement with those given by Snead and Clever (1962) while the pure CCl_4 values, like those of Vogel (1948) are higher than most values which can be obtained from literature data. The fact, that the values for CH_3NO_2 are slightly higher than the best literature values while the $C_2H_5NO_2$ values are equivalent to the best literature values implies that the slope of the CH_3NO_2 $\gamma-t$ function is changing more rapidly than usually accepted; the conclusion is not inconsistent with the possibility of slightly more evaporative loss at higher temperatures for the lower boiling CH_3NO_2. A greater variation is

TABLE 3.—Surface Thermodynamic Quantities.

Mole Fraction (RNO_2)	Entropy		Enthalpy					
			h_σ (ergs/cm²)			$h_m \times 10^{-10}$ (ergs/mole)		
	s_σ (ergs/cm²-deg)	$s_m \times 10^{-7}$ (ergs/mole-deg)	30°C	35°C	45°C	30°C	35°C	45°C
			Nitromethane					
0.0	0.133	20.0	66.9	66.7	66.9	10.8	10.8	10.8
0.1	0.137	20.3	68.4	68.2	68.4	10.8	10.8	10.8
0.2	0.137	19.6	68.6	68.2	68.5	10.5	10.4	10.5
0.3	0.124	16.6	64.8	64.6	64.8	9.46	9.44	9.46
0.4	0.128	16.5	66.3	66.0	66.2	9.33	9.28	9.32
0.5	0.107	11.8	59.8	59.4	59.7	7.76	7.68	7.75
0.6	0.103	10.4	58.9	58.8	58.9	7.19	7.17	7.19
0.7	0.107	10.1	60.8	60.8	60.8	7.05	7.03	7.04
0.8	0.120	11.1	66.0	66.2	66.0	7.34	7.36	7.34
0.9	0.133	12.5	72.0	72.4	72.1	7.85	7.89	7.87
1.0	0.172	17.8	87.7	87.1	87.6	9.71	9.64	9.70
			Nitroethane					
0.0	0.133	20.0	66.9	66.7	66.9	10.8	10.8	10.8
0.1	0.120	17.3	63.1	62.9	63.0	9.94	9.99	9.93
0.2	0.122	17.4	63.7	63.7	63.7	9.89	9.89	9.89
0.3	0.128	18.2	65.9	65.8	65.9	10.1	10.1	10.1
0.4	0.114	15.2	61.7	61.6	61.7	9.15	9.10	9.14
0.5	0.113	14.7	61.8	61.6	61.7	8.95	8.91	8.94
0.6	0.119	15.6	63.9	64.0	63.9	9.21	9.22	9.21
0.7	0.125	16.5	66.5	66.6	66.5	9.47	9.48	9.48
0.8	0.122	15.5	66.1	66.1	66.1	9.20	9.20	9.20
0.9	0.111	13.5	63.4	63.4	63.4	8.59	8.59	8.59
1.0	0.104	12.0	62.2	62.2	62.2	8.13	8.14	8.13

found for the molar thermodynamic quantities because of the variations in the density data. Both s_σ and s_m for nitromethane exhibit a minimum and, thus, indicates that the surface molecules of some nitromethane solutions are more ordered than the surfaces of either of the components. A possible explanation for the greater ordering would be the formation of a complex between CCl_4 and CH_3NO_2, a possibility diametrically opposed to the suggestions of de Maine *et al.* (1957) that a monomer-dimer nitroparaffin equilibrium occurs in these binary solutions. More likely, this effect is the demonstration previously unreported, for surface layers of the entropy of mixing effect, previously demonstrated for the bulk solutions of CCl_4 and CH_3NO_2 (Wettaw, *et al.* (1969)).

The surface entropies and enthalpies of mixing were calculated for each solution by taking the differ-

ence between a value in Table 3 and its corresponding value predicted for perfect solutions based upon additivity of components with respect to mole fraction. That is, the perfect solution value is found by replacing M_1 and M_2 in Equation (3) with the appropriate thermodynamic values, e.g. $(s_m)_1$ and $(s_m)_2$ to obtain $s_m{}^M$. Molar excess surface entropies of mixing, $s_m{}^E$, were calculated by addition of the terms

$$R \sum_{i=1}^{i=2} X_i \ln x_i$$

to the molar surface entropies of mixing, $s_m{}^M$. Scratchard (1949) has shown, for bulk solutions, that excess volume of mixing, V^E, can be fitted to a function of the form

$$V^E = a_0 x_1 x_2 + a_1 x_1 x_2 (x_1 - x_2) + \ldots\ldots\ldots \quad (4)$$

where a_0 and a_1 are constants, and

TABLE 4.—Surface Mixing and Excess Thermodynamic Quantities.

Mole Fraction (RNO_2)	Entropy			Enthalpy					
				M h_σ (ergs/cm²)			M $h_m \times 10^{-10}$ (ergs/mole)		
	M s_σ (ergs/cm²-deg)	M $s_m \times 10^{-7}$ (ergs/mole-deg)	E $s_m \times 10^{-7}$ (ergs/mole-deg)	30°C	35°C	45°C	30°C	35°C	45°C
Nitromethane									
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	0.0001	0.52	3.2	—0.58	—0.54	—0.57	0.11	0.12	0.11
0.2	—0.0038	0.04	4.0	—2.5	—2.6	—2.5	—0.08	—0.17	—0.08
0.3	—0.021	—2.7	2.3	—8.3	—8.2	—8.3	—1.0	—1.0	—1.0
0.4	—0.021	—2.6	3.0	—8.9	—8.9	—9.0	—1.0	—1.0	—1.0
0.5	—0.046	—7.1	—1.3	—18.	—18.	—18.	—2.5	—2.5	—2.5
0.6	—0.053	—8.3	—2.7	—20.	—20.	—20.	—3.0	—2.9	—3.0
0.7	—0.053	—8.4	—3.3	—21.	—20.	—21.	—3.0	—3.0	—3.0
0.8	—0.044	—7.1	—3.1	—18.	—17.	—17.	—2.6	—2.5	—2.6
0.9	—0.035	—5.5	—2.8	—14.	—13.	—13.	—2.0	—1.9	—1.9
1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nitroethane									
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	—0.010	—1.9	0.80	—3.3	—3.4	—3.4	—0.59	—0.63	—0.60
0.2	—0.0052	—1.0	3.0	—2.3	—2.1	—2.3	—0.38	—0.38	—0.38
0.3	0.0037	0.60	5.7	0.41	0.45	0.41	0.10	0.098	0.10
0.4	—0.0074	—1.6	4.0	—3.3	—3.3	—3.3	—0.58	—0.63	—0.59
0.5	—0.0055	—1.3	4.5	—2.8	—2.8	—2.8	—0.52	—0.56	—0.52
0.6	0.0034	0.40	6.0	—0.18	0.0	—0.18	0.012	0.016	0.012
0.7	0.012	2.1	7.2	2.9	3.0	2.9	0.54	0.54	0.55
0.8	0.012	1.9	5.9	3.0	3.0	3.0	0.54	0.53	0.54
0.9	0.0041	0.70	3.4	0.73	0.75	0.73	0.19	0.18	0.19
1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

x_1 and x_2 are the mole fraction of CCl_4 and nitroparaffin, respectively. For binary solutions, the first term on the right hand side of Equation (4) is a quadratic term in either x_1 or x_2 while the second term is a cubic term. Other molar excess quantities are expected, for bulk solution, to have the same functional form as Equation (4). Gunter *et al.* (1967) have shown for the bulk solutions of CH_3NO_2–CCl_4 that only a_0 is non-zero while for bulk solutions of $C_2H_5NO_2$–CCl_4 only a_1 is non-zero. The surface enthalpies of mixing, which are identical with the excess surface enthalpies of mixing, shown in Table 4 indicate exactly the same functional information. That is, the cubic functional forms of the nitroethane values represent less deviation from ideality than the quadratic functional form of the nitromethane values. The first example known to the present authors of the usual treatment of perfect solutions and excess functions to surface layers rather than to bulk solutions is given by Bloom, *et al.*(1960). Their application to molten salts is rather

TABLE 5.—Parachors of Carbon Tetrachloride-Nitroparaffin Solutions.

Mole Fraction (RNO_2)	Calculated from Solution Surface Tensions			Calculated from Component Surface Tensions			Calculated from Atomic and Bond Parachor Values
	30°C	35°C	45°C	30°C	35°C	45°C	
			Nitromethane				
0.0	222.0	221.3	221.8	222.0	221.3	221.8	229.8
.1	212.7	211.8	212.2	213.1	212.4	212.9	220.1
.2	203.4	202.5	202.9	204.3	203.6	204.0	210.3
.3	193.7	193.4	194.0	195.4	194.7	195.1	200.6
.4	184.5	184.0	184.9	186.5	185.8	186.3	190.9
.5	174.7	174.2	176.2	177.7	177.0	177.4	181.2
.6	165.2	165.2	167.2	168.8	168.1	168.5	171.4
.7	156.2	156.3	158.4	159.9	159.2	159.6	161.7
.8	147.9	148.3	149.9	151.1	150.4	150.8	152.0
.9	140.1	140.5	141.5	142.2	141.5	141.9	142.2
1.0	133.3	132.7	133.0	133.3	132.7	133.0	132.5
			Nitroethane				
0.0	222.0	221.3	221.8	222.0	221.3	221.8	229.8
.1	216.2	215.9	216.6	216.9	216.2	216.7	224.1
.2	210.8	210.6	211.0	211.8	211.2	211.7	218.3
.3	205.8	205.4	205.7	206.6	206.2	206.7	212.6
.4	200.2	198.6	200.6	201.5	201.2	201.6	206.9
.5	195.0	193.2	195.4	196.4	196.1	196.6	201.2
.6	189.8	190.0	190.1	191.2	191.1	191.6	195.4
.7	185.1	185.2	185.1	186.1	186.1	186.6	189.7
.8	180.4	180.3	180.5	181.0	181.0	181.5	184.0
.9	175.6	175.4	175.9	175.9	176.0	176.5	178.2
1.0	170.7	171.0	171.5	170.7	171.0	171.5	172.5

remote from the type of solutions discussed in this paper. The only other example of this treatment to surface layers known to the authors was published by Suri and Ramakrishna (1969) after the conclusion of the present work. However, the agreement with the conclusions of Gunter, *et al.* (1967) is a validation of the application to surface layers rather than an assumption that surface layers obey the same physical laws as the bulk solution.

The negative s_m^E nitromethane values indicate (Scatchard and Raymond (1938))that some CCl_4 molecules are associating with the clusters of nitromethane molecules, thus, substantiating the conclusion of ordered surfaces derived from the s_σ and s_m values. The positive s_m^E values indicate dissociation of the nitroparaffins. In one sense, both of the conclusioss suggested by Table 3 are valid, if a complex is interpreted as a simple association of molecules. Reid and Sherwood (1966) suggest the use of the parachor for the estimation of surface tensions of nonaqueous mixtures. Table 5 compares the values of the parachor calculated directly from solution densities and surface tensions and those calculated from the parachors of the mixture components. The maximum deviations of 2.3% (CH_3NO_2) and 1.5% ($C_2H_5NO_2$) from the linear mixture law indicate that estimation from parachor values is appropriate for these solutions. The greater deviations for the nitromethane solutions is attributed to the greater difference in surface tension of the components as first observed by Hammick and Andrew (1929). The discrepancy between the observed CCl_4 parachor value and the value obtained by addition of atomic parachors is attributed to the accumulation of negative groups (Mumford and Phillips (1929)) and suggests that a better estimation of surface tensions of carbon tetrachloride-nitroparaffin binary solutions would result from the use of an experimental CCl_4 parachor.

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TABLE 6.—Summary of Literature Values.

Surface Tension 30°C, γ (dyne/cm)	Entropy s_σ (ergs/cm²-deg)	Entropy $s_m \times 10^7$ (ergs/mole-deg)	Enthalpy h_μ (ergs/cm²)	Parachor [P]
Nitromethane				
34.26[2]	0.1387[7]	31.59[7]	81.1[4]	131.8[14]
35.47[3]	0.150[4]	15.8[5]	86.4[3]	132.6[3–8]
35.48[4]	0.1678[3]	14.4[3]	81.3[7]	132.7[7]
35.50[1]	0.160[5]	20.3[3]	84.4[5]	
35.9[5]	0.1464[8]		79.8[8]	
32.11*[2]				
Nitroethane				
31.5[3]	0.1090[7]	12.83[7]	69.8[8]	171.0[7–8]
	0.1255[3]	14.1[9]	65.7[9]	171.1[8]
	0.1163[9]	14.9[8]	67.1[7]	171.2[16]
	0.1218[5]	18.4[3]	67.9[8]	
Carbon Tetrachloride				
25.54[6]	0.119[4]	17.6[12]	61.7[4]	219.3[16]
25.57[4]	0.1259[10]	17.8[11]	63.6[10]	219.6[17]
	0.1327[5]	18.1[6]	66.5[8]	220.0[15]
	0.1173[11]	18.7[13]	60.5[11]	221.0[8]
		20.3[8]		
*45.1°C				

1. Suri and Ramakrishna (1969)
4. Hennaut-Roland and Lek (1931)
7. Boyd and Copeland (1942)
10. Pugachevich *et al.* (1963)
13. Morino (1932)
16. Ray (1934)
2. Morgan and Stone (1913)
5. Thompson *et al.* (1954)
8. Vogel (1948)
11. Ramsay and Aston (1894)
14. Hammick and Andrew (1929)
17. Mumford and Phillips (1950)
3. Snead and Clever (1962)
6. Harkins and Cheng (1922)
9. Ramsay and Shields (1893)
12. Renard and Guye (1907)
15. Mumford and Phillips (1929)

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