Thermodynamics of Liquid Surfaces

Surface Tensions of Eight High Purity Nitroparaffins from 0° to 60° C.

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SURFACE TENSIONS of nitromethane, nitroethane, 1-nitropropane, 1-nitrobutane, 2-nitropropane, 2-nitrobutane, and 1-nitro-2-methylpropane were determined at 10° intervals from 0° to 60° C. by the maximum bubble pressure technique. 2-Nitro-2-methylpropane surface tension was determined at 10° intervals between 30° and 60° C. by the same technique.

The nitroparaffin samples were prepared, purified, and sent in sealed ampules (Commercial Solvents Corp.). Their purity is the same as reported by Toops (*4*) in his determination of freezing points, boiling points, vapor pressures, densities, and refractive indices of the same nitroparaffins.

The surface tensions were determined by the maximum bubble pressure technique. The apparatus built and described by Quayle (*3*) was used. The temperature variation was ±0.1° at 0° and 10° C. and ±0.05° at the other temperatures. Necessary densities were extrapolated from the data of Toops (*4*).

Table I gives the experimental surface tensions, least squares slopes and intercepts for the straight lines, $\gamma = a - bt$, for each nitroparaffin (which reproduces the experimental values to ±0.06 dynes/cm.) and parachors.

Some surface tensions of five of the nitroparaffins were reported earlier by Boyd and Copeland (*1*) who used the ring method and by Vogel (*5*) who used the capillary rise method. The presently reported results are in approximate agreement but usually a bit higher than the earlier results. The higher values reported here are probably due to the use of samples of higher purity than were available before.

To form one square cm. of new surface (*6*) the free energy change is

$$(\partial F/\partial \Sigma)_{P,T} = \gamma \text{ ergs/sq.cm.}$$

the enthalpy change is

$$(\partial H/\partial \Sigma)_T = h = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_{P,\Sigma} \text{ ergs/sq.cm.}$$

the entropy change is

$$(\partial S/\partial \Sigma) = s = -\left(\frac{\partial \gamma}{\partial T}\right)_{P,\Sigma} \text{ ergs/deg./sq.cm.}$$

and the latent heat is

$$l = -T\left(\frac{\partial \gamma}{\partial T}\right)_{P,\Sigma} \text{ ergs/sq.cm.}$$

where γ is surface tension, Σ surface area, h the enthalpy change per square cm., s the entropy change per square cm., l the latent heat change per square cm., and the other symbols have their conventional thermodynamic significance.

Entropies, enthalpies, and latent heats in ergs/sq. cm. are given in Table II. Both entropy and enthalpy decrease as each methylene unit is added to the straight chain series.

Table I. Surface Tensions of Eight Nitroparaffins

Compound and Purity, Mole Fraction	Temperature, ° C.							Least Squares Constants		Parachor
	0	10	20	30	40	50	60	*a*	*b*	
Nitromethane, 99.99	40.67	39.12	37.48	35.47	34.02	32.34	30.72	40.72	0.1678	132.6 ± 0.2
Nitroethane, 99.9	35.46	33.88	32.66	31.50	30.24	28.95	27.83	35.27	0.1255	171.1 ± 0.4
1-Nitropropane, 99.7	32.55	31.68	30.64	29.61	28.48	27.66	26.53	32.62	0.1009	209.7 ± 0.8
2-Nitropropane, 99.99	32.14	31.08	29.87	28.68	27.54	26.41	25.22	32.18	0.1158	210.9 ± 0.4
1-Nitrobutane, 99.96	31.83	30.80	29.77	28.68	27.98	26.99	26.02	31.74	0.0959	248.0 ± 0.9
2-Nitrobutane, 99.9	31.77	30.50	29.48	28.40	27.36	26.30	25.18	31.70	0.1085	249.1 ± 0.4
1-Nitro-2-methyl propane, 99.82	30.34	29.42	28.37	27.49	26.46	25.80	24.45	30.35	0.0958	247.7 ± 0.6
2-Nitro-2-methyl propane, 99.9	...	...	...	27.38	26.30	25.28	24.26	30.48	0.1038	249.0 ± 0.5

Table II. Some Thermodynamic Properties of Surface Formation at 30° C.

	Entropy			Latent Heat	
	Ergs/deg./sq. cm.	Ergs/deg./mole $\times 10^{-7}$	Enthalpy Ergs/Sq. Cm.	Ergs/sq. cm.	Ergs/mole $\times 10^{-10}$
Nitromethane	0.1678	20.3	86.4	50.9	61.6
Nitroethane	0.1255	18.4	69.8	38.1	55.7
1-Nitropropane	0.1009	17.1	60.2	30.6	51.9
2-Nitropropane	0.1158	19.8	63.8	35.1	60.0
1-Nitrobutane	0.0959	18.3	57.8	29.1	55.4
2-Nitrobutane	0.1089	20.8	61.4	33.0	63.1
1-Nitro-2-methylpropane	0.0958	18.4	56.5	29.0	55.7
2-Nitro-2-methylpropane	0.1038	19.9	58.9	31.5	60.5

However, branching effects an increase in enthalpy over the value for the straight chain isomer. The trend in entropy seems to depend on whether the branching occurs on the carbon bearing the nitro group. For all the branched molecules, the carbon atom bearing the nitro group being branched results in a higher entropy than that of the straight chain isomer. In the one case where branching occurs on the carbon alpha to the nitro-bearing carbon, 1-nitro-2-methyl propane, however, the entropy of new surface formation is less than that of either 1-nitrobutane or 1-nitropropane.

Nitromethane appears to be anomalous in its surface thermodynamics. On the basis of one square cm. of surface, the entropy, enthalpy, and latent heat are much higher than for the other members of the series. If the thermodynamic properties are calculated on a molar basis by assuming spherical molecules and estimating molar surface area (square cm./mole) from

$$\Sigma = N^{1/3} V^{2/3}$$

where Σ is molar surface area, N is Avogadro's number and V is molar volume, the entropy and latent heat of nitromethane fits into the series without apparent anomaly. See the second columns under entropy and latent heat in Table II.

Parachor values are given in Table I. The increase in parachor with chain branching is the opposite of what is observed for hydrocarbons, alcohols, and halo paraffins (*3*). The increase in parachor, a molar volume under the corresponding state of unit surface tension, with chain branching in the highly polar and possibly dimerized nitroparaffins (*2*) may be evidence of a more ordered liquid than expected for the hydrocarbon and haloparaffin liquids.

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Thermodynamic Properties of Isobutylene

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EARLIER publications of the thermodynamic properties of isobutylene (2-methyl propene) (*4, 5*) have not only been quite limited in scope but also have involved approximations from using generalized correlations rather than rigorous techniques based on experimental data for this specific compound. Thermodynamic properties were calculated from selected experimental data for isobutylene from the literature. The calculations were based on rigorous thermodynamic relationships employing the Benedict-Webb-Rubin equation of state and were carried out using an electronic digital computer.

Values of pressure, volume, temperature, enthalpy, and entropy are presented for saturated liquid and vapor from 0° F. to the critical temperature, 292.5° F., and for superheated vapor for the region from 70° F. to 500° F. and from 1 atm. to 200 atm.

CHOICE OF DATUM

The datum state for both enthalpy and entropy was taken as identical with that used by the API Research Project 44 (*1*) and the National Bureau of Standards (*8*)—viz., the ideal gas state at absolute zero temperature and 1 atm., so that all values reported here are consistent with the values given in their tables for the ideal gas at 1 atm.

SUPERHEATED VAPOR

The enthalpy, H^0, and entropy, S^0, of the ideal gas at 1 atm. were first calculated for each isotherm by interpolation and extrapolation from the values listed in the tables of API Research Project 44. This was done using the heat capacity equation determined by Spencer (*9*) for the ideal gas.

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