Table III. Comparison of Calculated and Observed Values of ΔH_f° for Some Nitriles

	ΔH_f°, Calcd.	ΔH_f°, Obsd.
Acrylonitrile	45.6	43.7
Tri-CNE	123.6	123.9
TCNE	168.5	168.5
Fumaronitrile	78.2	81.3

Table IV. Groups and Their Contributions to Thermodynamic Properties in Nitriles

	Contribution	
Group	S°, Cal. Mole^{1} Deg.^{1}	ΔH_f°, Kcal. Mole^{1}
$C_t-(N_t)(C)$	30.00	...
$[C_t-(N_t)(C)] + [C-(H_2)(C)(C_t)]$	...	27.21
$[C-(H_2)(C_t)_2] - 2[C-(H_2)(C)(C_t)]$	...	9.08
$2[C_t-(N_t)(C_d)] + [C_d-(C_t)_2(C_d)]$	...	83.75
$[C_t-(N_t)(C_d)] + [C_d-(H)(C_t)(C_d)]$	...	39.33

tion of group *B* to ΔH_f°, which was 39.33 kcal. per mole. The results of using this value are shown in Table III.

The values given for the calculated and observed values of ΔH_f° for TCNE are the same. This agreement results, of course, from the fact that the contribution of group *A* was determined from the observed value of ΔH_f° for TCNE, which is composed entirely of two of these *A* groups. The correlation is not as satisfactory as that given in Table II, but nevertheless, the estimated values agree to 3% or better with the observed values. That the correlation is less satisfactory in Table III than in Table II may be attributed to various possible causes. Since there is no reason to suspect that ΔH_f° values will be inherently less reliable than s° values, it does not seem reasonable to suggest this as a major factor. However, all compounds in Table III have been decomposed into one or more groups, to each of which is assigned a contribution to ΔH_f°. In addition, all groups contain at least two of the type of group found in Table II. Hence, it may well be that the numbers assigned to the group contributions are in error by a factor of two or more when compared with the simpler groups of Table II. However, the most intriguing possible explanation of the difference in correlation errors relates to a difference in the nature of the molecules of Table II and those of Table III. The molecules of Table II are largely composed of bonds with which localized electrons are usually associated, while a substantial amount of delocalization of electrons can reasonably be attributed to the molecules of Table III. It is not unreasonable to suggest that such delocalization over the entire molecular framework may render partitioning less accurate than in the case of localized bonds.

CONCLUSION

A satisfactory correlation of heats of formation and absolute entropies of nitriles was obtained by employing the groups and values listed in Table IV.

LITERATURE CITED

(1) Benson, S.W., Buss, J.H., *J. Chem. Phys.* **29**, 546 (1958).
(2) Boyd, R.H., *Ibid.*, **38**, 2529 (1963).
(3) Boyd, R.H., Guha, K.R., Wuthrick, R., *J. Phys. Chem.* **71**, 2187 (1967).
(4) Clever, H.L., Wulff, C.A., Westrum, E.F., Jr., *Ibid.*, **69**, 1983 (1965).
(5) Crowder, G.A., Cook, B.R., *Ibid.*, **71**, 914 (1967).
(6) Davis, H.S., Weideman, O.F., *Ind. Eng. Chem.* **37**, 482 (1945).
(7) Moffat, J.B., *Can. J. Chem.* **42**, 1323 (1964).
(8) Moffat, J.B., *Chem. Comm.* **1966**, p. 789.
(9) Moffat, J.B., Collens, R.J., *Can. J. Chem.* **45**, 655 (1967).
(10) Moffat, J.B., Popkie, H.E., *Intern. J. Quantum Chem.* to be published.
(11) Popkie, H.E., Moffat, J.B., *Can. J. Chem.* **43**, 624 (1965).
(12) Rapport, N., Westrum, E.F., Jr., private communication in (*3*).
(13) Ribner, A., Westrum, E.F., Jr., *J. Phys. Chem.* **71**, 1208 (1967).
(14) Roberts, J.S., Skinner, H.A., *Trans. Faraday Soc.* **45**, 339 (1949).
(15) Rossini, F.D., *Natl. Bur. Std. Circ.* **500** (1952).
(16) Westrum, E.F., Jr., Ribner, A., *J. Phys. Chem.* **71**, 1216 (1967).
(17) Wulff, C.A., Westrum, E.F., Jr., *Ibid.*, **67**, 2376 (1963).

RECEIVED for review July 20, 1967. Accepted October 24, 1967. The financial assistance of the National Research Council of Canada is gratefully acknowledged.

Sulfur–Naphthalene–*n*-Octadecane System

T. K. WIEWIOROWSKI and B. L. SLATEN
Freeport Sulphur Co., Belle Chasse, La. 70037

Phase equilibria in a ternary system consisting of molten sulfur, naphthalene, and *n*-octadecane were investigated at 113° C. Experimental data were obtained by infrared absorption measurements. The phase diagram indicates that, contrary to recent literature, molten sulfur is quite selective when considered as a solvent with respect to the other two components. The direction of the tie lines indicates that naphthalene can be preferentially extracted by molten sulfur from a mixture of the two hydrocarbons.

THIS study was undertaken in an effort to establish whether molten sulfur can exhibit any selectivity toward one hydrocarbon over another one in a ternary system. A recent paper (*2*), reporting phase diagrams of 15 ternary systems of elemental sulfur, concludes that in every case tried, all tie lines pointed directly toward the sulfur corner, indicating that in all of these systems, molten sulfur is characterized by a complete lack of solvent selectivity. The present investigation deals with a ternary system of sulfur, naphthalene, and *n*-octadecane—that is, a system which, although not identical, is very similar to that represented by phase diagram 11 in reference (*2*). Although the general shapes of the solubility curves are quite alike in both cases, the directions of the tie lines are not. This gives rise to the new conclusions concerning the selectivity of molten sulfur presented in this paper.

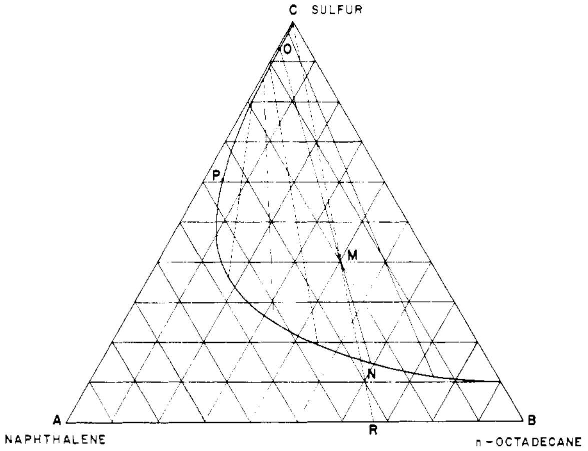

Figure 1. Sulfur–naphthalene–*n*-octadecane phase diagram at 113° C.

EXPERIMENTAL

The sulfur used in this study was purified by the method of Bacon and Fanelli (*1*). Naphthalene was white label grade from Eastman Organic Chemicals and *n*-octadecane (olefin-free grade) was obtained from Humphrey-Wilkinson, Inc.

A series of sulfur–naphthalene–*n*-octadecane mixtures was prepared, the compositions of which are presented in Table I. In most cases, the ratio of sulfur to *n*-octadecane was 1 to 1, while the naphthalene fraction was varied. Fifty grams of each mixture were agitated in a separatory funnel at 113° ± 1° C. The ternary mixtures were allowed to separate into two equilibrated liquid phases, one octadecane rich (top phase), and the other sulfur rich (bottom phase). The two phases were separated, allowed to cool, and weighed.

A portion of the sulfur phase was diluted with pure sulfur and melted. The dilution factor was 9-to-1 or 19-to-1 depending upon the concentration of the organic components in the sulfur phase. This diluted sulfur phase was analyzed by infrared spectrophotometry using heated cells with a 1/32-inch light path (*3*). The concentration of naphthalene and *n*-octadecane was calculated from the infrared absorbancies by referring to previously established calibration curves.

The calibration curves were prepared by dissolving known amounts of naphthalene and octadecane in molten sulfur and plotting the absorbancies at 3070 and 2920 cm.$^{-1}$, respectively, *vs.* concentration.

The analysis of the octadecane rich phase was accomplished by obtaining infrared spectra in carbon tetrachloride solution. Conventional 0.15-mm. sodium chloride infrared cells were used for this purpose. Again, the concentrations of both organic components were determined from calibration curves, which in this case were prepared using carbon tetrachloride as the solvent. Because of differences in concentrations and absorptivities of naphthalene and octadecane, different dilution factors were required for their determination. The reproducibility of infrared analyses was in all cases better than 2% of the amount present.

The compositions of both phases determined in this manner on the investigated series of ternary mixtures are presented in Table I, from which the ternary phase diagram (Figure 1) was prepared.

DISCUSSION

A ternary system consisting of components *A*, *B*, and *C* may be regarded as being composed of three binary systems *A*-*B*, *A*-*C*, and *B*-*C*. The system, which is the subject of the present investigation, belongs to the most common type of ternary systems—that is, one in which two of the binary systems consist of completely miscible components, and the third binary system is one in which the components are only partially miscible. In the present case, the systems sulfur-naphthalene and naphtalene–normal octadecane are completely miscible, while the system sulfur–normal octadecane is only partially miscible. The naphthalene, therefore, may be considered as being distributed in the ternary system between two liquid phases, one consisting primarily of molten sulfur and the other consisting primarily of normal octadecane.

The ternary phase diagram (Figure 1) can be interpreted in terms of the solvent selectivity of molten sulfur with respect to a mixture of the other two components. Consider a mixture of naphthalene and normal octadecane represented by point *R* on the phase diagram. Addition of sulfur to this mixture will gradually change the composition of the system along the straight line *RC* toward the sulfur apex. Suppose the addition of sulfur is discontinued at point *M*, and the system is allowed to equilibrate. The system will separate into two phases, the compositions of which are defined by points *O* and *N*. The ratio of naphthalene to normal octadecane is obviously much higher in the sulfur-rich phase (point *O*) than it is either in the feed (point *R*) or in the octadecane-rich phase (point *N*). On the basis of data presented in Table I, it can be calculated that, for original naphthalene-octadecane ratios ranging from 0.22-to-1 to 3.29-to-1, the corresponding ratios in the sulfur phase vary from 8.67-to-1 to 18.10-to-1. Consequently, molten sulfur is selective with respect to naphthalene in this system. Repetitive extraction of the octadecane-rich phase with molten sulfur will result in a gradual depletion of its naphthalene content.

The direction of tie lines is of particular significance in the interpretation of ternary phase diagrams. The selectivity of molten sulfur for naphthalene in the system is reflected by the fact that the tie lines do not point toward the sulfur apex. The finding that molten sulfur exhibits selectivity toward naphthalene in this system is not surprising. Since naphthalene is miscible with molten sulfur in any proportion, while *n*-octadecane is only slightly soluble in molten sulfur, one would actually expect to observe a certain degree of solvent selectivity in the ternary system. This finding is in direct opposition to the results reported

Table I. Analytical Data for the Sulfur-Naphthalene-Octadecane System at 113° C.

Test	Orig. Comp., Wt. %			Sulfur-Rich Phase, %			Octadecane-Rich Phase, %		
No.	C_{18}	Naph.	S	C_{18}	Naph.	S	C_{18}	Naph.	S
1	50	0	50	0.13	0	99.87	90.0	0	10.0
2	45	10	45	0.30	2.60	97.10	72.9	13.9	13.2
3	40	20	40	0.30	6.10	93.60	58.5	26.5	15.0
4	35	30	35	0.60	10.40	89.00	44.3	35.3	20.4
5	30	40	30	0.94	13.50	85.56	33.0	42.7	24.3
6	14	40	46	1.00	18.10	80.90	17.8	46.1	36.1

in previous literature (*2*). On previously reported phase diagrams of ternary molten sulfur systems, the tie lines point directly to the sulfur corner indicating that sulfur has no selectivity for either of the other two components.

The results presented in this paper suggest that molten sulfur may be a useful solvent for the separation of certain mixtures by extraction. On the basis of the limited amount of experimental data available, it is difficult to define exactly the types of mixtures which could be separated by extraction with molten sulfur. Apparently, however, cyclic organic compounds, and in particular aromatic, unsaturated and basic organic compounds, could be removed from saturated open-chain hydrocarbons by solvent extraction with sulfur. For example, continuous countercurrent contact of a naphthalene–normal octadecane mixture with molten sulfur would yield an octadecane phase saturated with sulfur but free of naphthalene and a molten sulfur phase containing dissolved naphthalene and minute quantities of octadecane.

LITERATURE CITED

(1) Bacon, R.F., Fanelli, R., *Ind. Eng. Chem.* **34**, 1043 (1942).
(2) Francis, A.W., J. CHEM. ENG. DATA **11**, 557 (1966).
(3) Wiewiorowski, T.K., Matson, R.F., Hodges, C.T., *Anal. Chem.* **37**, 1080 (1965).

RECEIVED for review August 11, 1967. Accepted September 18, 1967.

Thermal Conductivity of Fluids. Propane

L. T. CARMICHAEL, JOAN JACOBS, and B. H. SAGE
Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif. 91109

Measurements of the thermal conductivity of propane were carried out at pressures up to 5000 p.s.i.a. in the temperature interval between 40° and 340° F. The data were obtained with a conductivity cell of spherical section and are in satisfactory agreement with the data of other investigators obtained with instruments of markedly different configuration. The results are presented in graphical and tabular form. So far as can be ascertained, the residual thermal conductivity appears to be a single-valued function of specific weight throughout the range of conditions covered in the investigation except in the critical region. No detailed study of the latter region was made.

AS a result of limited information concerning the thermal conductivity of propane (*11-13, 23, 28-30, 32*), and continuing uncertainty as to the extent to which the residual thermal conductivity can be considered a single-valued function of the specific weight, measurements of the thermal conductivity of propane were made in the temperature interval between 40° and 340° F., at pressures between atmospheric and 5000 p.s.i.a.

Some progress has been made in predicting the thermal conductivity of the lighter hydrocarbons at attenuation (*4, 13, 24, 30*). However, it has not yet proved particularly effective to apply the principles of statistical mechanics to the prediction of the thermal conductivity of the lighter hydrocarbons at pressures markedly above that of the atmosphere. The thermal conductivity in the critical region was not investigated in detail.

EQUIPMENT AND METHODS

A conductivity cell of spherical section was employed in these investigations (*18-20*). This equipment involved a gold-plated sphere approximately 3.5 inches in diameter placed symmetrically within a slightly larger spherical cavity. The radial transport path was approximately 0.020 inch between the inner sphere and the outer shell. The inner sphere was provided with a specially-designed electrical heater that yielded nearly equal flux at all points around the surface of the sphere (*19*). Small thermocouples were employed to establish the temperature of the inner spherical surface of the outer shell. Appropriate corrections were made for the location of the thermocouples within the stainless steel body of the sphere and of the shell (*18*). Dimensions of the spherical cavity and the inner sphere were determined by direct physical measurements, and appropriate corrections for changes in the length of the transport path with changes in temperature and pressure were made. These corrections, for the most part, did not amount to much more than 1.0% in the resulting value of thermal conductivity. To check the over-all performance of the equipment, measurements upon the thermal conductivity of helium and argon at atmospheric pressure (*5, 6, 8*) were made. Comparisons yielded satisfactory agreement with values (*6, 8, 16, 31*) that are known with relatively high accuracy.

At most states, measurements were carried out at four different values of thermal flux. Periods of as much as 8 hours, but mostly approximately 4 hours, were required to achieve a steady state at each level of thermal flux. Values of $(q_m/d\theta)/\Delta t_m$ were established for each thermocouple at each level of flux. Individual corrections for the location of the thermocouples below the surface of the sphere and of the shell were applied after the limiting value at zero flux of the aforementioned derivative was obtained by application of regression analysis to the points as a group.

As a result of the change in average temperature of the phases with some local convection possible, there was a significant variation in the apparent thermal conductivity with flux, and the onset of gross convection could be easily established by rapid increase in the apparent thermal conductivity with a small increase in the radial temperature gradient. Measurements were made under such conditions that gross convection in the transport path was not experienced. In the above-described regression analysis, the authors assumed that the change in the apparent thermal conductivity or of the derivative, $(q_m/d\theta)/\Delta t_m$, was linear