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Effects of Temperature and of Mixing on Dielectric Constants of Several Organic Solvents

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It is known that the dielectric constants of the organic solvents are dependent on temperature[1] and that those of binary mixtures are not usually equal to the calculated average values.[2] In other words, the curve obtained by plotting the dielectric constants of mixtures against the molar fraction of one of the components usually shows some curvature. Although much data have been obtained for organic solvents and their binary mixtures at different temperatures, relatively little has been reported on hydrocarbons, inert solvents and their mixtures, which are often used for studies on autoxidation. In the course of our study on the solvent effects in autoxidation,[3,4] we have determined the dielectric constants of tetralin, several inert solvents and their mixtures at temperatures from 25°C to 70°C.

The measured dielectric constants for several pure liquids at different temperatures are summarized in Table 1 together with the values in literature.[5] As a whole, the observed values show good agreement with the reported values. Table 1 shows that the dielectric constants for 9 out of 10 liquids decrease with an increase in temperature. The only exception is that for butyric acid, which increases with an increase in temperature.

Lowry and Jessop[6] found that the following correlation exists between the dielectric constants of liquids and temperature.

$$D = D_0 \exp(-LT) \quad (1)$$

where D_0 and L are constants characteristic for each liquid. The equation

$$\log(D_1 D_2) = L(T_2 - T_1)/2.303 \quad (2)$$

is derived from Eq. (1). In Fig. 1, the logarithm of D_1/D_2 is plotted as a function of $(T_2 - T_1)$ using the measured dielectric constants in Table 1 assuming T_1 to be 298°K. Figure 1 shows that Eq. (2) holds for all the solvents measured. The calculated values of L from the slope of the lines in Fig. 1 for each liquid are given in the last column of Table 1. The value of L varies with solvents by a factor of more than 7. The liquid with high

TABLE 1. DIELECTRIC CONSTANTS AT DIFFERENT TEMPERATURES AND THE VALUES OF L FOR 10 PURE LIQUIDS

Liquid	Dielectric constants measured at					D(°C)[a]	$L \times 10^3$
	25°C	40°C	50°C	60°C	70°C		
n-Decane	2.011	1.986	1.977	1.960	1.949	1.991(20)	0.696
Benzene	2.297	2.278	2.254	2.229	2.200	2.284(20)	0.957
Tetralin	2.771	2.737	2.709	2.686	2.657	2.757(20)	0.931
Butyric acid	2.949	2.977	3.011	3.029	3.063	2.97 (20)	−0.839
Butylstearate	3.120	3.051	3.000	2.949	2.909	3.111(30)	1.57
Anisole	4.331	4.194	4.097	4.000	3.926	4.33 (25)	2.18
Chlorobenzene	5.583	5.366	5.211	5.057	4.909	5.621(25)	2.85
Diethyl maleate	7.560	7.251	7.034	6.834	6.623	8.58 (23)	2.93
Acetophenone	17.48	16.14	15.34	14.63	13.98	17.39 (25)	4.96
Nitrobenzene	34.42	32.05	30.20	28.71	27.35	34.82 (25)	5.12

a) Literature values.[5]

1) E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd Ed., Oxford University Press, London (1947), p. 90; "Physical Chemistry," Pergamon Press, London (1957), p. 853.

2) J. Timmermans, "Physico-chemical Constants of Binary Systems in Concentrated Solutions," Interscience, New York (1959).

3) E. Niki, Y. Kamiya and N. Ohta, This Bulletin in contribution.

4) E. Niki, Y. Kamiya and N. Ohta, *ibid.*, in contribution.

5) J. A. Riddick and E. E. Toops, Jr., "Technique of Organic Chemistry," Vol. VII, "Organic Solvents," ed. by A. Weissberger, Interscience, New York (1955).

6) T. M. Lowry and G. Jessop, *Trans. Chem. Soc.*, **1930**, 782.

Table 2. Dielectric constants for the binary mixtures of tetralin and various solvents at 70°C[a)]

Solvent	Tetralin, vol%				
	80	60	40	20	0
n-Decane	2.514	2.360	2.206	2.069	1.949
Butyric acid	2.674	2.743	2.834	2.937	3.063
Butyl stearate	2.697	2.743	2.806	2.857	2.909
Anisole	2.874	3.126	3.377	3.651	3.926
Chlorobenzene	3.086	3.509	4.017	4.440	4.909
Diethyl maleate	3.360	4.126	4.943	5.811	6.623
Acetophenone	4.269	6.269	8.589	11.21	13.98
Nitrobenzene	6.126	10.27	15.02	21.10	27.35

a) *D* for pure tetralin at 70°C is 2.657.

Table 3. Dielectric constants for the systems tetralin-nitrobenzene-solvent at 70°C
Tetralin=20 vol%

Solvent	Nitrobenzene/Solvent, vol/vol				
	1/0	3/1	1/1	1/3	0/1
n-Decane	21.10	14.84	9.846	5.503	2.069
Chlorobenzene	21.10	15.63	11.43	7.720	4.440
Acetophenone	21.10	18.42	15.65	13.35	11.21

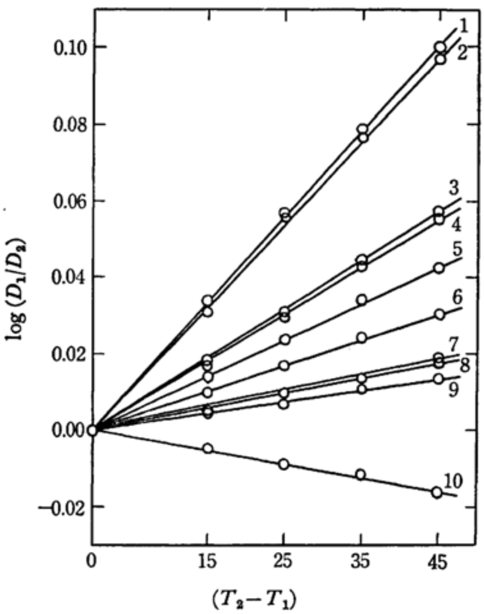

Fig. 1. Variation of dielectric constant with temperature.
1. Nitrobenzene 6. Butyl stearate
2. Acetophenone 7. Benzene
3. Diethyl maleate 8. Tetralin
4. Chlorobenzene 9. *n*-Decane
5. Anisole 10. Butyric acid

dielectric constant gives a large value for *L*. It is interesting that the value of *L* for butyric acid is negative in contrast to other liquids.

The dielectric constants for the mixtures of tetralin and various inert solvents were measured at 70°C and the results are summarized in Table 2. As shown in Fig. 2, the plots of the dielectric constants against tetralin concentration give upward

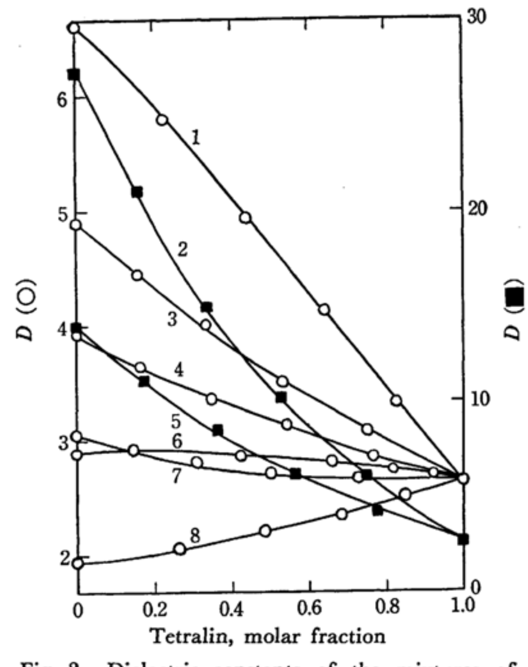

Fig. 2. Dielectric constants of the mixtures of tetralin and solvents at 70°C.
1. Diethyl maleate 5. Acetophenone
2. Nitrobenzene 6. Butyl stearate
3. Chlorobenzene 7. Butyric acid
4. Anisole 8. *n*-Decane

and downward convex curves. In Table 3 are summarized the dielectric constants for the systems of tetralin-nitrobenzene-solvents at 70°C. These values again gave convex curves when plotted as a function of the tetralin concentration.

Experimental

Tetralin, *n*-decane and chlorobenzene were washed successively with sulfuric acid, water, alkali, and water, dried with calcium chloride, and then distilled under reduced pressure of nitrogen. Anisole and nitrobenzene were washed with alkali and water, dried and distilled under reduced pressure. Diethyl maleate and acetophenone were fractionally distilled. Butyric acid and butyl stearate of guaranteed grade were used without further purification. The water content in butyric acid was less than 0.1%.

The dielectric constants were measured at 2Mcps of frequencies using a Dielectric Analyzer Model FAM-3A, Yamato Scientific Instrument Co. Two kinds of dielecric cells were used, one for the solution of low dielectric constant (smaller than 20) and the other for the high dielectric solution (larger than 20). The cell constants for the two cells were determined with several solvents as standard. Since the same apparatus and technique have been used in this study, errors in the measurements will be relative and will not affect the general nature of the conclusion drawn.