Part II

Density and Surface Tension of Phenol, (Mono-, Di-, and Tri-) chlorophenols, Salol, and (*o*- and *m*-) Chloronitrobenzenes

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Densities and surface tensions of phenol, *m*- and *p*-chlorophenols, 2,4-dichlorophenol, 2,4,5-trichlorophenol, salol, and *o*- and *m*-chloronitrobenzenes in the liquid state have been measured at different temperatures around their melting points. The data for both above and below the melting points can be represented by a single straight line indicating a continuous change of such properties as these liquids go from the normal to the supercooled liquid states.

MANY physical properties of a substance show remarkable changes or discontinuities during transition from liquid to solid state. During this transition, an intermediate metastable supercooled liquid state is often encountered which plays an important role in the nucleation and crystallization process. Compounds with closely related chemical structures show widely different supercooling tendencies. In the present investigation, data have been obtained on densities and surface tensions of eight related organic compounds at different temperatures in their normal and supercooled liquid states. No such detailed data on these compounds are available in the literature.

EXPERIMENTAL

All of the compounds as obtained in the pure reagent grade were subjected to fractional distillation and crystallization under prescribed procedures, and the middle fraction was used for experimental work after careful drying.

Density Measurements. Densities (d) at the appropriate temperatures were determined with a Lipkin-type (*6*) pycnometer. The level of liquids in the two arms above the reference mark was more accurately measured with a travelling microscope reading to ±0.001 cm. It was calibrated with double distilled water at different temperatures in a thermostat controlled to ±0.01° C. All weighings were accurate to ±0.00005 gram and the density values better than ±0.0001.

Surface Tension. The surface tension (γ) was determined by the capillary rise method (*4*). The value of the surface tension of water as measured with this apparatus and values found in the literature were in good agreement. The reproducibility of results was better than ±0.05 dynes per cm.

Temp.	Observed S.T., Dynes/Cm.	Literature Value, Dynes/Cm.
26.0	71.96	71.82
30.0	71.32	71.18
40.0	69.65	69.56
50.0	68.00	67.91

In all cases, the measurements for the molten compounds were started at the lowest temperature and then subsequently at higher temperatures.

The experimental data are presented in Table I.

Table I. Densities and Surface Tensions of Compounds at Different Temperatures Around Their Melting Points

T., ° C.	Density, Gm./Cc.	S.T., Dynes/Cm.	T., ° C.	Density, Gm./Cc.	S.T., Dynes/Cm.
	Phenol			2,4,5-Trichlorophenol	
28.0	1.0685	40.50	58.0	1.5233	. . .
30.0	1.0669	40.33	60.0	1.5208	41.33
32.0	1.0651	40.11	62.0	1.5182	41.14
34.0	1.0634	39.93	64.0	1.5156	40.91
36.0	1.0617	39.74	66.0	1.5131	40.69
38.0	1.0602	39.53	68.0	1.5116	40.46
40.0	1.0584	39.21	70.0	1.5079	40.23
42.0	1.0567	39.05	72.0	1.5053	40.01
44.0	1.0549	38.90	74.0	1.5028	39.76
46.0	1.0532	38.64	76.0	1.5003	39.58
48.0	1.0515	38.42	78.0	1.4972	39.33
50.0	1.0497	38.19	80.0	. . .	39.10
52.0	1.0480	37.93			
	m-Chlorophenol			Salol	
20.0	. . .	42.78	30.5	1.1911	42.21
22.0	1.2743	42.48	32.5	1.1893	42.07
24.0	1.2722	42.29	35.0	1.1868	41.68
26.0	1.2712	42.04	37.5	1.1846	41.47
28.0	1.2691	41.82	40.0	1.1822	41.22
30.0	1.2663	41.66	42.5	1.1802	41.19
32.0	1.2652	41.39	45.0	1.1779	40.92
34.0	1.2630	41.25	47.5	1.1757	40.61
36.0	1.2603	41.13	50.0	1.1736	40.29
38.0	1.2582	40.80	52.5	1.1713	40.12
40.0	1.2572	40.60	55.0	1.1692	39.83
42.0	1.2540	40.37	60.0	1.1649	39.24
	p-Chlorophenol			*o*-Chloronitrobenzene	
28.0	1.2727	44.14	23.0	1.3682	44.80
30.2	1.2701	43.91	25.0	1.3658	44.55
32.0	1.2689	43.63	27.0	1.3637	44.34
34.0	1.2674	43.44	29.0	1.3614	44.20
36.0	1.2653	43.21	31.0	1.3592	43.98
38.0	1.2633	42.98	33.0	1.3567	43.75
40.0	1.2613	42.75	35.0	1.3547	43.63
42.0	1.2593	42.52	37.0	1.3527	43.25
44.0	1.2573	42.29	39.0	1.3503	43.06
46.0	1.2554	42.06	41.0	1.3480	42.74
48.0	1.2533	41.83			
50.0	1.2512	41.60			
	2,4-Dichlorophenol			*m*-Chloronitrobenzene	
34.0	1.4137	. . .	38.0	1.3529	42.33
36.0	1.4113	. . .	40.0	1.3503	42.14
38.0	1.4088	41.97	42.0	1.3479	41.95
40.0	1.4062	41.72	44.0	1.3458	41.76
42.0	1.4039	41.47	46.0	1.3436	41.58
44.0	1.4014	41.22	48.0	1.3414	41.39
46.0	1.3989	40.97	50.0	1.3392	41.20
48.0	1.3966	40.72	52.0	1.3371	41.01
50.0	1.3942	40.47	54.0	1.3349	40.82
52.0	1.3917	40.22	56.0	1.3326	40.64
54.0	1.3891	39.99			
56.0	1.3867	39.76			

Table II. Least Square Values of Slopes (*m*) and Intercepts (*c*) to the Equation (d or γ) = $c - mT$

	Density		Surface Tension	
Compound	*c*	*m*	*c*	*m*
Phenol	1.0968	0.000862	43.54	0.1068
m-Chlorophenol	1.2913	0.000828	44.82	0.1055
p-Chlorophenol	1.2951	0.000844	47.41	0.1164
2,4-Dichlorophenol	1.4557	0.001233	46.65	0.1235
2,4,5-Trichlorophenol	1.5984	0.001293	48.04	0.1222
Salol	1.2177	0.000883	45.20	0.0976
o-Chloronitrobenzene	1.3916	0.001049	47.37	0.1107
m-Chloronitrobenzene	1.3948	0.001111	45.89	0.0939

DISCUSSION

The plots (not shown) illustrate that the variation of density (or specific volume) *vs.* temperature, over regions of 10° to 15° C. below and above the melting points, shows a linear relationship. The least square value of the slopes (m) and intercepts (c) of the equation (d or γ) = $c - mT$ are given in Table II. If there were any differences in the packing density between the normal and the supercooled liquid states as a result of a change in structure or nature of vibration (from rotational to oscillational), it was not detected, at least, within the present degree of accuracy in measurement of density.

Similar studies were made by Moore and coworkers (*7*) on TNT-picric acid and related systems; by Greenwood and Martin (*3*) on complexes of borontrifluoride with acetic acid and its esters; and by Dodd (*1*) on phenyl ether. All these did not show any discontinuity at or near the transition point from the normal to the supercooled state, indicating that the transition is not of the first order. Discontinuity in the plot of $[(1/V)(dV/dT)]$ *vs.* T would indicate a second order transition. However, the authors' plot showed such a scattering that no definite conclusion can be made.

Surface tension behavior was investigated to check whether structural changes, if any, owing to supercooling extended to the surface. Also, a property such as interfacial tension enters in the nucleation and growth equations as an important factor.

The plots of γ *vs.* T also showed a linear relation for all the compounds similar to that observed by Dodd and Mi (*2*). The least square c and m values are noted in Table II. The authors have also calculated a few surface thermodynamic quantities using the surface tension data, as mentioned.

To form 1 sq. cm. of a new surface, the changes in free energy, enthalpy (h), entropy (s), and latent heat (l), respectively, are given (*5*) by

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

Table III. Calculated Surface Thermodynamic Properties of Compounds at Their Melting Points

Compound	T., ° C.	$\frac{1}{V}\cdot\frac{dV}{dT}\times 10^4$	M.P.	*S*, Ergs/Sq. Cm.	*H*, Ergs/Sq. Cm.	*L*, Ergs/Sq. Cm.	Eötvös Constant
Phenol	41.0	9.09	39.16	0.1068	72.70	33.54	1.75
m-Chlorophenol	32.8	6.54	41.36	0.1055	73.54	32.18	1.56
p-Chlorophenol	40.0	6.69	42.75	0.1164	79.18	36.43	2.10
2,4-Dichlorophenol	45.0	8.81	41.09	0.1235	80.33	39.24	1.20
2,4,5-Trichlorophenol	67.0	8.35	39.89	0.1222	81.44	41.55	1.13
Salol	42.1	7.48	41.09	0.0976	71.84	30.75	. . .
o-Chloronitrobenzene	32.5	7.72	43.44	0.1107	77.25	33.81	. . .
m-Chloronitrobenzene	44.4	8.25	41.72	0.0939	71.5	29.80	. . .

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

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

and

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

where A is the surface area. The values of h, s and l below and above the melting point do not differ significantly because of the same value of $(\partial\gamma/\partial T)$ in the two regions. However, for a comparison of their individual values, the melting point has been taken as the reference point, and the corresponding data are assembled in Table III. It appears that significant differences exist between the *m*- and *p*-chlorophenols and also between *m*- and 2,4-dichlorophenols in their enthalpy and latent heat values. Also, a similar difference is noticeable in the case of *o*-chloro- and *m*-chloronitrobenzene.

The Eötvös constants [slope of the plot of $\gamma(M/d)^{2/3}$ against temperature] for phenol and chlorophenols are given in the last column of Table III.

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Ternary Systems of Acetonitrile

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This paper presents experimental graphs of 19 aqueous and 97 nonaqueous ternary systems of acetonitrile. Also included are 34 quaternary systems plotted as triangular graphs, with the extra component assigned as a diluent to one of the other three components. The purpose of the research was to observe effects of diluents on selectivity, gross solubility, and elimination of isopycnics, which are otherwise prevalent in acetonitrile systems. Carbon disulfide is the most effective cosolvent for these functions. The graphs exhibit a wide variety of features with isopycnics, twin density lines, iso-optics, an island curve, and two and three separate binodal curves, as well as the usual types.

ACETONITRILE has high selectivity for certain types of hydrocarbon. It has a convenient boiling point, 82°, and low melting point, −42°. Development as a commercial selective solvent was retarded by its excessive cost, now considerably reduced. It also presents two technical difficulties: It dissolves very low volumes of high molecular weight hydrocarbons in the lubricating oil range; and it has a low density, 0.7824, which is close to those of some of the hydrocarbons to be treated. Thus, there is a risk of isopycnics or systems of two layers of equal density.

Both of these difficulties can be overcome by the use of appropriate cosolvents. For example, dilution of the hydrocarbon mixture with carbon disulfide increases the density considerably, so that the acetonitrile-rich layer is definitely the upper one (*14*). Carbon disulfide has only a moderate mutual miscibility with acetonitrile; but its mixtures with lubricating oils and other hydrocarbons are appreciably more soluble in acetonitrile than without the diluent. Other cosolvents of either high or low density may be employed similarly. Carbon tetrachloride, though with higher density, is less effective than carbon disulfide for preventing isopycnics, because it is more evenly distributed. On the other hand, it may be satisfactory for the other purposes.

Critical solution temperatures (CST) have been listed for acetonitrile with about 37 hydrocarbons and with nearly 50 nonhydrocarbons (*4*, pp. *17–19*). Only a few ternary systems of acetonitrile have been published previously, not all with graphs. These are aqueous systems of ethylene (*2*), heptane (*16*), and trichloroethylene (*17*); and nonaqueous systems of benzene-heptane (*16*), ethane-ethylene (*1*), heptane-methylcyclohexane or 2-methyl-2-butene (*3*), and toluene-methylcyclohexane (*3*).

The general purpose of this investigation was to find novel methods of combining solvents for improved separation of hydrocarbon mixtures. Some systems studied are reflected in patents (*12–15*). Silver nitrate, which has a strong affinity for lower olefins, is almost as soluble in acetonitrile as it is in water; but acetonitrile contrasts with water in being miscible with the liquid olefins (graph 91). Various combinations of the two solvents permit considerable flexibility, provided the cost of the silver is tolerable.

This paper presents in graphic form (Figure 1) experimental observations on 150 new systems of acetonitrile, most of them ternary, and most of them with at least two

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