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## Equations of state approach for interpretation of contact angles

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### Abstract

The determination of solid surface tensions from existing static contact angles has been especially considered. On supposition of the constancy of the surface tension for a given solid surface, experimental contact angle patterns are employed to calculate solid-vapor surface tension ( $\gamma_{sv}$ ) with the equation of state of Antonow [1], the equation of state of Berhtloet's with three different approaches one with the combining rule [2], the second with the modified [3] combining rule and the third with the use of a different modifying factor [4] and by the use of the equation of state of Neumann, *et al.* [5].

**Keywords:** Equations of state, Contact angles, liquid vapour interfacial tensions and Zisman plot

### 1. Introduction

In 1805, Thomas Young (1773-1829) and Pierre-Simon Laplace (1749-1827) introduced the concept of surface tension. In 1970, Josiah W Gibbs (1839-1903) suggested the idea of free surface energy. Thermodynamically, the free surface energy is given by the difference of the Gibbs free energy and Helmholtz free energy. Instead of direct measurement of surface tension of solid phase, it is better to measure it indirectly because of involved uncertainties in direct measurements. The various approaches for indirect measurement of surface tension of solid phase used are: contact angles [6-8, 13, 14, 17], the gradient theory [9-11, 26, 27], the theory of molecular interactions [12-14, 31-33], Lifshitz theory of van der Waals force [15-17, 42,43,45], direct force measurements [18-20], solidification front interaction with particles [21-23,27, 24, 25], and capillary penetration into columns of particle powder [21-22; 18, 20, 21]. Contact angle measurements are of fundamental importance in everyday processes and in industrial use. Contact angle measurement is easily carried out by knowing the tangent (angle) of a liquid drop with solid surface at the base. Let us take a look at a liquid drop on a solid surface. Three types of interfaces can be distinguished in this system: the interface between the solid surface and the surrounding gas (air), the interface between the liquid and the gas (air), and the interface between the solid surface and the liquid. The surface tensions at these interfaces are  $\gamma_{sv}$ ,  $\gamma_{lv}$ , and  $\gamma_{sl}$ , respectively. The line along which all the three interfaces intersect is referred to as the line of wetting. The angle between the liquid-gas and solid-liquid interfaces,  $\theta$ , is referred to as the contact angle.

The liquid-vapour surface tension times, cosine of the contact angle  $\gamma_{lv} \cos \theta$ , is shown to depend only on the liquid-vapour surface tension,  $\gamma_{lv}$  and the solid-vapour surface tension,  $\gamma_{sv}$ . Accordingly, the vectorial summation of these interfacial tensions at the three phase intersection point (three phase contact point) gives

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta_e \quad (1)$$

Here, the contact angle  $\theta_e$  is not a constant quantity, but unique. For advancing liquid, it is  $\theta_a$  and for retarding liquid it is  $\theta_r$ . The difference between the two is the hysteresis,

$$H = \theta_a - \theta_r \quad (2)$$

Where  $\gamma$  is the surface tension term, SV denotes solid/vapor, SL stands for solid/liquid and lv is for liquid/vapor interfaces as seen in the Figure 1.

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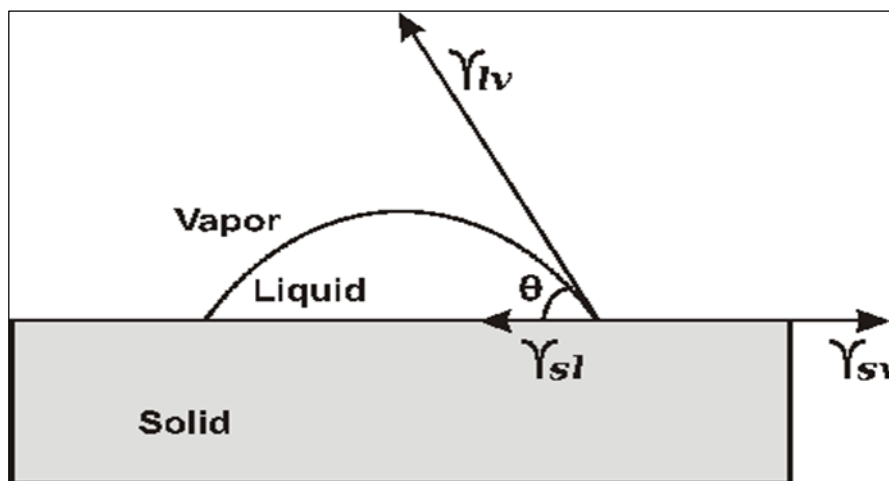


Fig 1: Contact angle system

Since,  $\gamma_{sl}$ ,  $\gamma_{sv}$ ,  $\gamma_{lv}$  are thermodynamic properties of the liquid and solid. The data for the values of solid-liquid interfacial tension ( $\gamma_{sl}$ ), the solid-vapour interfacial tension ( $\gamma_{sv}$ ) and the liquid-vapour interfacial tension ( $\gamma_{lv}$ ) has a wide range of scientific and industrial uses. The contact angle measurements on solids reflect the thermodynamics of liquid-solid interactions. The measurements of surface tension of the solid can be ascertained with the knowledge of the data of contact angles. This is why one first determines the contact angles on the solid surface by spreading drops of series of liquids. However, exact physical meaning of contact angles has not been studied clearly, and it is also not understood that the wetting is controlled either by the intersections through the total solid/liquid contact area or only at the three phase contact line (solid/liquid/gas) formed around the droplet. This appeared as a new concept for the surface free energy of solids. In theoretical part, we are giving the mathematical expressions for the equations of state approach to calculate the solid surface tension of solids. In section 2, the values of the known dynamic contact angles of these solids which were determined by ADSA-P (automated axis symmetric drop shape analysis-profile) method are tabulated in Table 1. Table

2 presents the calculated values for solid surface tension,  $\gamma_{sv}$  for these solids using five different equations of state (7), (11), (13), (15), and (17). Fig. 1-5 has been plotted for  $\gamma_{lv} \cos \theta$  versus  $\gamma_{lv}$ . Section 3 presents Table 3 in which contact angles of solid surfaces which were determined from Zisman *et al.* goniometric technique instead of ADSA-P technique. Table 4 also contains the values of  $\gamma_{sv}$  using the five different equations of state ((7), (11), (13), (15), and (17)). The Zisman method of plot (Figs.6-8) has been used to know  $\gamma_c$  or  $\gamma_{sv}$ . Section 4 includes the results and discussion part, and finally section 5 deals with conclusion of this work. Before dealing with the equations of state we will first present here definition of solid air interfacial energy  $\gamma_{sv}$  of solid surfaces.

### 1.1 Interaction energy of solid surfaces

The solid-air interfacial energy  $\gamma_{sv}$  of solid surfaces is akin to the liquid-air interfacial tension of liquids, and its unit is the same  $Nm^{-1}$ . It may be defined as the force per unit length acting perpendicularly to the surface of a solid. The other definition of this is the change in the total surface free energy

G per unit change in surface area A at constant temperature T,

$$\gamma_{sv} = \left( \frac{\partial G}{\partial A} \right)_{T,P,n}$$

pressure P and moles n, i.e.,

and therefore its unit is sometimes expressed in  $Jm^{-2}$ . The Young equation, which describes the force balance between the solid surface energy, liquid surface energy, and solid-liquid interfacial energy when a liquid drop is placed on a solid surface can be used to estimate the value of the solid surface energy provided the other two forces and the equilibrium contact angle are known. But, the real problem is in the estimation of the solid-liquid interfacial energy, though various mathematical models have been used to estimate it. The approaches that are used are in given by two-models: the surface tension component approach and the equation of state approach. According to the first approach,  $\gamma_{sl}$  depends on  $\gamma_{lv}$  and  $\gamma_{sv}$ , as well as the specific intermolecular interactions, i.e., components of the surface energy. The second, however says,  $\gamma_{sl}$  depends only on  $\gamma_{lv}$  and  $\gamma_{sv}$  and a thermodynamic relation of the type  $\gamma_{sl} = F(\gamma_{lv}, \gamma_{sv})$  exists.

### 1.2 Equation of state approach

The equation of state approach has been used successfully to calculate the surface tension of solids for flat surfaces where only the effects of the tensions involved are dominant. Based on the thermodynamic approach, the interfacial tensions are related by an equation of state. It has been concluded that the values of  $\gamma_{lv} \cos \theta$  depend only on  $\gamma_{lv}$  and  $\gamma_{sv}$ , independent of any specific intermolecular forces of the liquids and solids [35, 36]:

$$\gamma_{lv} \cos \theta = f(\gamma_{lv}, \gamma_{sv}) \quad (3)$$

Where  $f$  is an unknown function. Combining Young's equation with equation (3) gives

$$\gamma_{sv} - \gamma_{sl} = f(\gamma_{lv}, \gamma_{sv}), \text{ therefore} \quad (4)$$

$$\gamma_{sl} = \gamma_{sv} - f(\gamma_{lv}, \gamma_{sv}) = F(\gamma_{lv}, \gamma_{sv}) \quad (5)$$

Where F is another constant and relation (5) is found to exist thermodynamically.

### 1.2.1 Equation of state approach: Antonow's rule

According to Antonow's a relation for  $\gamma_{sl}$  of following type, which mathematical derivation never exists, is given by:

$$\gamma_{sl} = |\gamma_{la} - \gamma_{sa}| \quad (6)$$

Combining this rule with the equation of state of Young's, we have:

$$\cos \theta_Y = -1 + 2 \frac{\gamma_{sv}}{\gamma_{lv}} \quad (7)$$

Thus,  $\gamma_{sv}$  can be determined, when  $\gamma_{lv}$  and  $\theta_Y$  are known.

Once  $\gamma_{sv}$  is known,  $\gamma_{sl}$  can be found either from equation (7) or from Young's equation (1).

### 1.2.2 Equation of state approach: Bertholet's geometric mean combining rule

Use of Bertholet's combining rule, gives another equation of

state. The dispersion energy coefficients  $C_6^{ij}$  are written in terms of  $C_6^{ii}$  and  $C_6^{jj}$  as  $C_6^{ij} = (C_6^{ii} C_6^{jj})^{0.5}$ , where  $I$  and  $J$  represent the phases, in the treatment of London theory of dispersion forces is used as basis. It appears in the similar form as that of the relation used for potential energy parameters (well depth) for like and unlike interactions

( $\epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}}$ ). Bertholet's assumed that the interfacial work of adhesion  $W_{sl}$  is equal the geometric mean of the cohesion work  $W_{ss}$  of a solid and cohesion work  $W_{ll}$  of the liquid. i.e.,  $W_{ls} = (W_{ss} W_{ll})^{0.5}$  where by definition,  $W_{ss} = 2\gamma_{sv}$  and  $W_{ll} = 2\gamma_{lv}$ . However, thermodynamically,

$$W_{sl} = \gamma_{sa} + \gamma_{la} - \gamma_{sl} \quad (8)$$

$$W_{sl} = 2(\gamma_{lv} \gamma_{sv}) \quad (9)$$

Equation (8) and (9) together yields

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2(\gamma_{lv} \gamma_{sv})^{0.5} = (\sqrt{\gamma_{lv}} - \sqrt{\gamma_{sv}})^2 \quad (10)$$

Equation (10) and Young's equation together yields

$$\cos \theta_Y = -1 + 2 \sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} \quad (11)$$

Thus, the solid-vapor interfacial surface tension can be determined when experimental contact angle and liquid-vapor interfacial surface tension are known.

### 1.2.3 Equation of state approach: modified Bertholet's rule

The equation of state for solid-liquid interfacial tensions using the modified Bertholet's rule ( $\epsilon_{ij} = (1 - K_{ij}) \sqrt{\epsilon_{ii} \epsilon_{jj}}$ ) can be written as:

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2(\gamma_{lv} \gamma_{sv})^{0.5} e^{-\beta(\gamma_{lv} - \gamma_{sv})^2} \quad (12)$$

Equation (12) together with Young's equation (1), we have

$$\cos \theta_Y = -1 + 2 \sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} e^{-\beta(\gamma_{lv} - \gamma_{sv})^2} \quad (13)$$

Thus, the solid surface tensions can be determined from the known value of Young's contact angle (experimental) and liquid surface tensions. The value of  $\beta$  is a constant quantity which has been determined by Newton's method and found to be  $\beta = 0.0001247 (m^2 / mJ)^2$ .

### 1.2.4 Equation of state approach: modified Bertholet's rule with an alternative formulation:

The alternative equation of state for solid-liquid interfacial tensions using the new modified Bertholet's rule

$$\left( \epsilon_{ij} = \left( 1 - K_1 (\epsilon_{ii} - \epsilon_{jj})^2 \right) \sqrt{\epsilon_{ii} \epsilon_{jj}} \right) \text{ can be written as:}$$

$$\cos \theta_Y = \gamma_{lv} + \gamma_{sv} - 2 \sqrt{\gamma_{lv} \gamma_{sv}} \left( 1 - \beta_1 (\gamma_{lv} - \gamma_{sv})^2 \right) \quad (14)$$

Equation (14) together with Young's equation (1), we have

$$\cos \theta_Y = -1 + 2 \sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} \left( 1 - \beta_1 (\gamma_{lv} - \gamma_{sv})^2 \right) \quad (15)$$

Where  $\beta_1 = 0.0001057 (m^2 / mJ)^2$

### 1.2.5 Equation of state of Neumann

The equation of state formulated by Neumann with the use of Good's interaction parameter

$$\Phi \left( \Phi = (\gamma_{sv} + \gamma_{lv} - \gamma_{sl}) / 2 \sqrt{\gamma_{lv} \gamma_{sv}} \right) \text{ as:}$$

$$\gamma_{sl} = \frac{(\sqrt{\gamma_{lv}} - \sqrt{\gamma_{sv}})^2}{1 - 0.015 \sqrt{\gamma_{lv} \gamma_{sv}}} \quad (16)$$

Equation (16) together with Young's equation (1), we have

$$\cos \theta_Y = \frac{(0.015 \gamma_{sv} - 2.00) \sqrt{\gamma_{lv} \gamma_{sv}} + \gamma_{lv}}{\gamma_{lv} (0.015 \sqrt{\gamma_{lv} \gamma_{sv}} - 1)} \quad (17)$$

Equation (17) is also known as Neumann-Zisman equation of state.

**1. Data (surfaces of four solids and forty two liquids Data for contact angles  $\theta$ , and the liquid vapour interfacial tensions,  $\gamma_{lv}$  by ADSA-P technique**

**Table 1:** The dynamic contact angles of various solids by ADSA-P method [37]

Solid surface/technique	Liquid	$\theta$ (degree)	$\theta$ (radian)	$\gamma_{lv}$ ( $mJ / m^2$ )
FC-722-Coatedmica/ADSA-P	Decane	67.36	1.176	23.88
	1-Petanol	72.95	1.273	26.01
	Trans-Decalin	73.38	1.281	27.19
	Hexadecane	75.94	1.325	27.62
	1-Decanol	78.84	1.376	28.90
	cis-Decalin	79.56	1.389	32.32
	Ethyl cinnamate	86.54	1.510	37.17
	Dibenzylamine	90.70	1.583	40.80
	Dimethyl sulfoxide	90.95	1.587	42.68
	1-Bromonaphthalene	93.81	1.637	44.31
	Diethylene glycol	94.22	1.644	44.68
	Ethylene glycol	97.87	1.708	47.55
	Diiodomethane	101.18	1.766	49.98
	2, 2'-Thiodiethanol	104.56	1.825	56.26
	Formamide	108.49	1.894	59.08
FC-725-coated silicon water/ADSA-P	Glycerol	111.73	1.950	65.02
	Water	118.69	2.072	72.70
	Dodecane	71.02	1.24	25.64
	Hexadecane	73.41	1.281	27.62
	3, 3-Thiodipropanol	90.48	1.579	39.83
	Diethylene glycol	94.47	1.649	45.16
	Ethylene glycol	100.05	1.746	48.66
	2,2'-Thiodiethanol	101.07	1.764	53.77
Teflon (FEP)/capillary rise	Formamide	106.89	1.866	59.08
	Glycerol	110.21	1.924	63.13
	Water	119.31	2.082	72.70
	Dodecane	47.8	0.834	25.03
	2-Octanol	52.3	0.913	26.00
	Tetradecane	52.6	0.918	26.50
	1-Octanol	54.4	0.949	27.28
	Hexadecane	53.9	0.941	27.31
	1-Hexadecane	54.2	0.946	27.75
Poly (methyl methacrylate)/ADSA-P	1-Dodecane	55.7	0.972	29.53
	Dimethylformamide	68.6	1.197	35.21
	Methyl salicylate	72.2	1.260	38.85
	1, 3-Diiodopropane	36.95	0.645	46.51
	3-Pyridylcarbinol	39.47	0.689	47.81
	Diiodomethane	42.25	0.737	49.98
	2, 2'-Thiodiethanol	50.35	0.879	53.77
FC-722-Coatedmica/ADSA-P	Formamide	57.73	1.008	59.08
	Glycerol	66.84	1.167	65.02
	Water	73.72	1.287	72.70

**Table 2:** The calculated values from equations of state [37].

Solid surface/technique + Liquid	$\gamma_{sv}$ EOS (7)	$\gamma_{sv}$ EOS (11)	$\gamma_{sv}$ EOS (13)	$\gamma_{sv}$ EOS (15)	$\gamma_{sv}$ EOS (17)
<b>FC-722-Coatedmica/ADSA-P</b>					
+ Decane	16.5361	11.4508	11.8702	11.8116	11.9372
1-Petanol	16.8181	10.8746	11.4639	11.3836	11.5428
Trans-Decalin	17.4834	11.2420	11.9156	11.8248	11.9866
Hexadecane	17.1649	10.6674	11.3916	11.2948	11.4724
1-Decanol	17.3004	10.3245	11.1749	11.0633	11.2578
cis-Decalin	19.0882	11.2735	12.4412	12.2937	12.4837
Ethyl cinnamate	19.7066	10.4479	12.2050	12.0013	12.2029
Dibenzylamine	20.1507	9.9522	12.2038	11.9628	12.1471
Dimethyl sulfoxide	20.9861	10.3191	12.8778	12.6144	12.7704
1-Bromonaphthalene	20.6828	9.6542	12.4378	12.1665	12.3097
Diethylene glycol	20.6960	9.5865	12.4270	12.1527	12.2909
Ethylene glycol	20.5195	8.8549	12.1119	11.8307	11.9244
Di-iodomethane	20.1446	8.1193	11.7011	11.4279	11.4720
2,2'-Thiodiethanol	21.0582	7.8821	12.6625	12.4149	12.2539

Formamide	20.1717	6.8872	11.9772	11.8061	11.5250
Glycerol	20.4737	6.4468	12.7448	12.7466	12.1542
Water	18.8994	4.9131	12.2299	12.7675	11.5789
<b>FC-725-coatedsilicon water/ADSA-P</b>					
+Dodecane	16.9895	11.2576	11.8078	11.7324	11.8802
Hexadecane	17.7530	11.4109	12.1159	12.0213	12.1837
3,3- Thiodipropanol	19.7481	9.7913	11.8950	11.6655	11.8621
Diethylene glycol	20.8201	9.5987	12.5200	12.2424	12.3722
Ethylene glycol	20.0842	8.2896	11.6626	11.3886	11.4647
2,2'-Thiodiethanol	21.7228	8.7759	13.2238	12.9336	12.8588
Formamide	20.9575	7.4343	12.7097	12.5131	12.2351
Glycerol	20.6604	6.7615	12.7377	12.6613	12.1796
Water	18.5554	4.7359	11.9051	12.4623	11.2555
<b>Teflon(FEP)/capillary rise +</b>					
Dodecane	20.9215	17.4875	17.7220	17.6884	17.7307
2-Octanol	20.9498	16.8806	17.2091	17.1628	17.2199
Tetradecane	21.2977	17.1167	17.4685	17.4190	17.4770
1-Octanol	21.5801	17.0712	17.4846	17.4270	17.4913
Hexadecane	21.7004	17.2431	17.6492	17.5925	17.6548
1-Hexadecane	21.9912	17.4276	17.8581	17.7983	17.8613
1-Dodecane	23.0854	18.0473	18.5937	18.5189	18.5855
Dimethylformamide	24.0286	16.3980	17.7010	17.5368	17.6450
Methyl salicylate	25.3631	16.5582	18.3819	18.1642	18.2676
<b>Poly(methylmethacrylate)/ADSA-P + 1,3-</b>					
Diiodopropane	41.8394	37.6379	38.2792	38.1942	38.2637
3-Pyridylcarbinol	42.3586	37.5288	38.3719	38.2626	38.3604
Diiodomethane	43.4880	37.8393	38.9953	38.8500	39.0071
2,2'-Thiodiethanol	44.0402	36.0710	38.2919	38.0356	38.3751
Formamide	45.3116	34.7520	38.5886	38.1931	38.9769
Glycerol	45.2961	31.5555	37.9058	37.3549	39.0539
Water	46.5400	29.7933	39.3304	38.6785	44.0125

## 2. Data (surfaces of three solids and seventeen liquids) for contact angles $\theta$ , and the liquid vapour interfacial tensions, $\gamma_{lv}$ by Goniometric technique

**Table 3:** Shows the contact angle and the interfacial tension data  $\gamma_{lv}$  of three solid surfaces [37]

Solid surface/technique	Liquid	$\theta$ (degree)	$\theta$ (radian)	$\gamma_{lv}$ ( $mJ/m^2$ )
17-(perfluoropropyl)-heptadecanoic acid	Perfluoroalkane (FCD-330)	23.0	0.927	20.2
	Bis-(2-ethylhexyl) phthalate	60.0	0.500	31.3
	Dicyclohexyl	62.0	0.469	32.8
	Tricetyl phosphate	72.0	0.309	40.9
	Ethylene glycol	84.0	0.105	47.7
	Methylene iodide	86.0	0.070	50.8
	Water	106.0	-0.276	72.8
Paraffin	Std. fluorolube	38.0	0.782	25.1
	Formamide	91.0	-0.017	58.2
	Glycerol	96.0	-0.105	63.4
	Water	108.0	-0.309	72.8
17-(Perfluoroethyl)-heptadecanoic	Dicyclohexyl	61.0	0.485	32.8
	Tricetyl phosphate	72.0	0.309	40.9
	Ethylene glycol	80.0	0.174	47.7
	Methylene iodide	83.0	0.122	50.8
	Formamide	94.0	-0.070	58.2
	Water	105.0	-0.259	72.8

**Table 4:** Shows the calculated values of  $\gamma_{sv}$  by using the five different types of equations of state described in section 1 [37]

Solid surface/technique + Liquid	$\gamma_{sv}$ EOS (7)	$\gamma_{sv}$ EOS (11)	$\gamma_{sv}$ EOS (13)	$\gamma_{sv}$ EOS (15)	$\gamma_{sv}$ EOS (17)
17-(perfluoropropyl)-heptadecanoic acid + Perfluoroalkane (FCD-330)	19.3970	18.6261	18.6374	18.6357	18.6384
Bis-(2-ethylhexyl) phthalate Dicyclohexyl Tricetyl phosphate Ethylene glycol Methylene iodide	23.4750	17.6062	18.3573	18.2569	18.3382
	24.0993	17.7066	19.3070	19.1938	19.2709
	26.7693	17.5207	19.6163	19.3722	19.4615
	26.3430	14.5482	18.1010	17.7544	17.8090
	27.1718	14.5336	18.7709	18.3905	18.4101

Water	26.3668	9.5495	19.4307	19.5028	19.1765
Paraffin + Std. florolube	22.4395	20.0610	20.1824	20.1647	20.1832
Formamide	28.5921	14.0465	20.1537	19.7366	19.6838
Glycerol	28.3864	12.7096	20.2350	19.8720	19.7522
Water	25.1517	8.6897	18.2514	19.8720	19.7522
17-(Perfluoroethyl)-heptadecanoic+Dicyclohexyl	24.3508	18.0782	18.9624	18.8459	18.9275
Tricresyl phosphate	26.7693	17.5207	19.6163	19.3722	19.4615
Ethylene glycol	27.9915	16.4260	19.9140	19.5632	19.6212
Methylene iodide	28.4954	15.9841	20.1913	19.8021	19.8365
Formamide	26.9789	12.5908	18.6123	18.2277	18.1156
Water	45.2961	31.5555	37.9058	37.3549	39.0539

### 3. Result and discussion

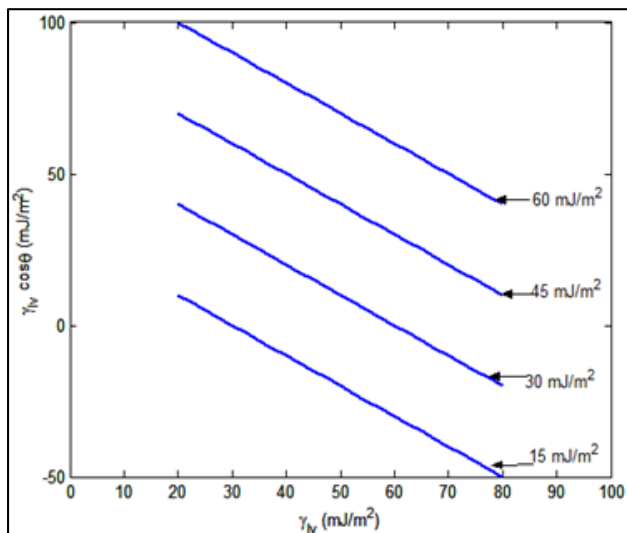


Fig 1:

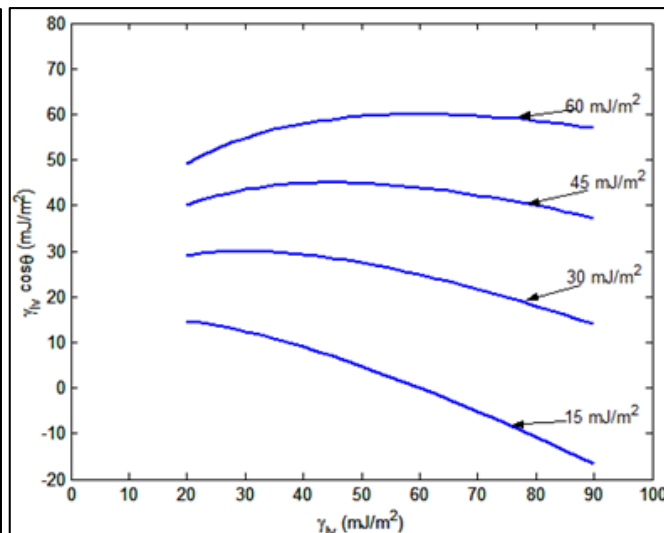


Fig 2:

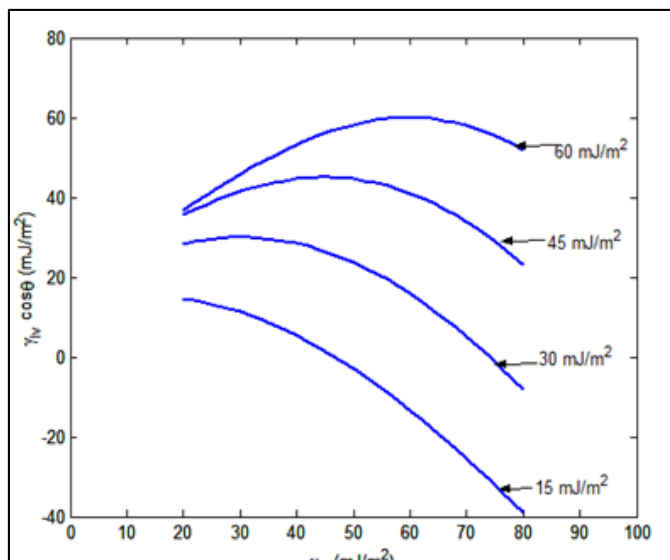


Fig 3:

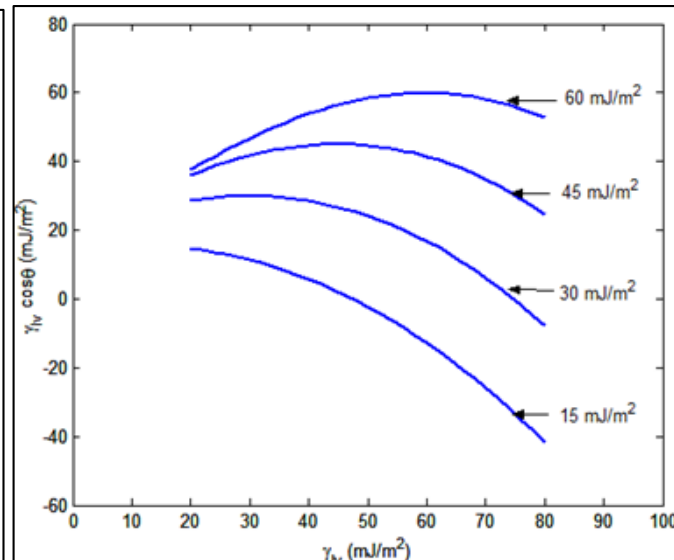
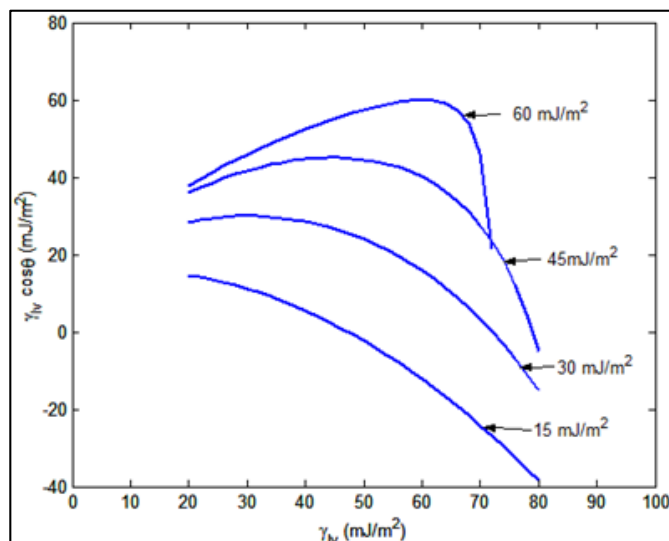


Fig 4:





**Fig 5:** Fig 1-5  $\gamma_{lv} \cos \theta$  vs.  $\gamma_{lv}$  generated from the equations of state approach with Eqs (7)

Eqs. (11), (13), (15) and (17), from  $\gamma_{sv} = 15 \text{ mJ/m}^2$  to  $\gamma_{sv} = 60 \text{ mJ/m}^2$ , in  $\gamma_{sv} = 15 \text{ mJ/m}^2$  increments.

For our study we have selected from literature the values of contact angles, and liquid-vapour interfacial tensions of the following solid surfaces with liquids. With the use of an automated ADSA-P technique the contact angles for the solid surfaces with the selected liquids were determined by co-workers. Out of their work, we have selected: FC-722-Coated mica with 17 liquids; FC-725-coated silicon water with 9 liquids; Teflon with 9 liquids; Poly (methyl-methacrylate) with 4 liquids. The values of contact angles and liquid air interfacial tension for this set are given in Table 1 of section 2. The other set for the values of contact angle of the selected three solid surfaces with the selected liquids are given in Table 2 of section 3. For this the co-workers used goniometer technique. These are: 17-(perfluoropropyl)-heptadecanoic acid with 7 liquids; Paraffin with 4 liquids and 17-(Perfluoroethyl)-heptadecanoic<sup>[133]</sup> with 6 liquids. The three equations i.e., the equation (13), equation (15) and equation (17) nearly results the same value of solid-vapour interfacial tension for any combination of solid surface + liquid and when calculated with the known value of interfacial tension and contact angle. The average value of the solid-vapour interfacial tension for any combination from these three equations can be regarded as an exact constant for  $\gamma_{sv}$ . The relative deviation of this constant  $\gamma_{sv}$  as calculated from Young equation has been found more than 20%. Fig. 1-5 implies that  $\gamma_{lv} \cos \theta$  depends only on  $\gamma_{lv}$  at constant  $\gamma_{sv}$ . Each of these figures represents the predictive power of the equation of state approach will be illustrated simply by predicting, from a single contact angle measurement, all the other contact angles measured on one and the same solid surface. It can be concluded that the values of  $\gamma_{lv} \cos \theta$  depend only on  $\gamma_{lv}$  and  $\gamma_{sv}$ , independent of any specific intermolecular forces of the liquids and solids. A plot of  $\cos \theta$  vs.  $\gamma_{lv}$  results the same as that of the plot of  $\gamma_{lv} \cos \theta$  vs.  $\gamma_{lv}$ . The equations of state approach for solid-liquid interfacial tensions can be used to evaluate these data by generating a series of theoretical constant curves ( $\gamma_{sv}$ ) in plots of  $\gamma_{lv} \cos \theta$  vs.  $\gamma_{sv}$ .

The Zisman plot, which is actually the Fox and Zisman observations, is an empirical technique used widely in industry. The Zisman method is used to obtain the critical surface tension value of solid. The outcome of the Zisman experiment was that when a dispensed liquid spreads freely on the surface if its surface tension is less than or equal to the surface tension of the solid. It had been also observed by him that critical surface tension occurs when the surface tension value of a liquid is equal to the surface tension value of a solid. Liquids with surface tension below the  $\gamma_c$  value spread on the solid surface.

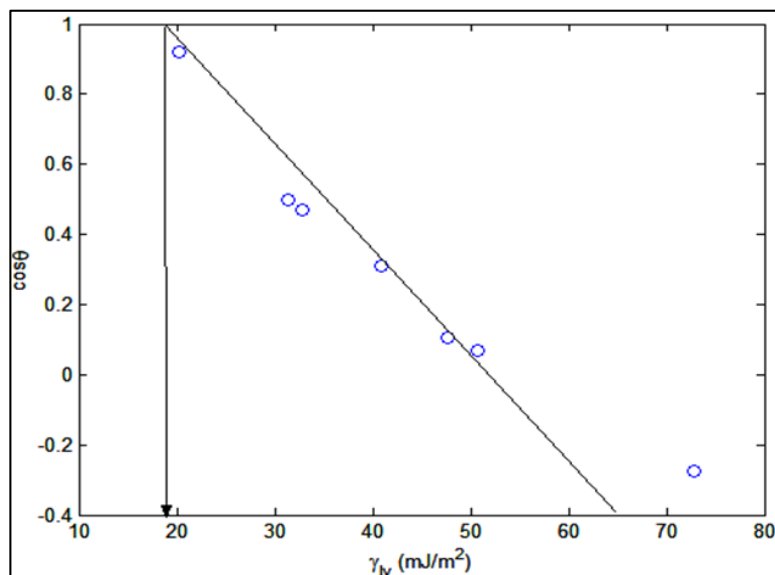
The Zisman plot is a representation of the interfacial surface tensions ( $\gamma_{lv}$ ) of different liquids that are plotted against the cosine of their contact angle to obtain the line of best fit. This line can be extrapolated to  $\cos \theta = 1$  (i.e.,  $\theta = 0^\circ$ ) to give the value of the 'critical surface tension'  $\gamma_c$  of the solid, where a liquid will just completely wet the surface,  $\gamma_{lv} < \gamma^{crit}$ . It has been observed that  $\gamma_c$  is a reasonable approximation for  $\gamma_{sv}$ , that means it is a semi-empirical parameter and is not the surface tension of the solid, although it is close to this value.

It is often not unreasonable to equate  $\gamma_c$  with  $\gamma_{sv}$ , because in many cases at complete wetting  $\gamma_{sl}$  approaches zero. We would expect a liquid to spread on a substrate if:  $S_{ls} = \gamma_{sv} - \gamma_{lv} - \gamma_{sl} > 0$  where,  $S_{ls}$  is called the spreading coefficient. If  $S_{ls} > 0$ , the liquid will spread. The wetting can be described by the Young equation

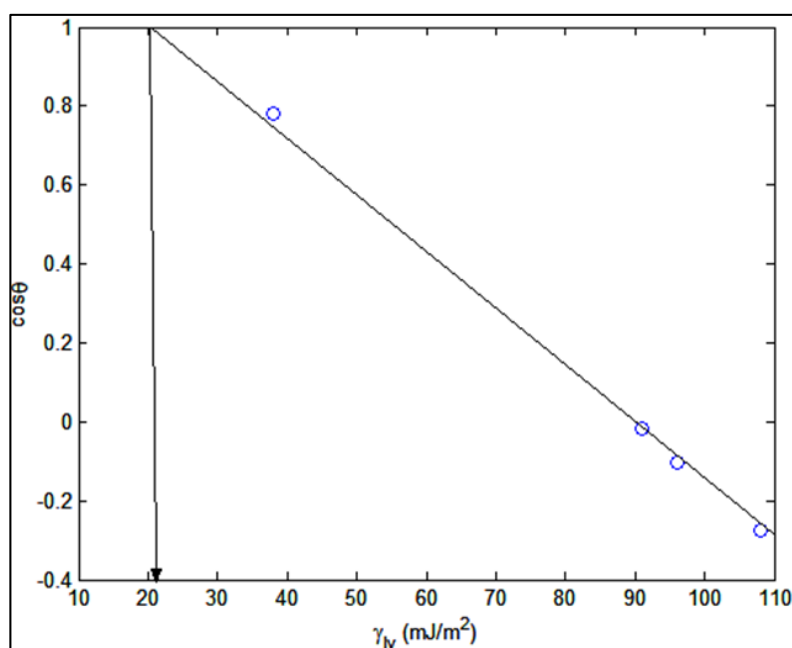
$$\gamma_s = \gamma_{sl} - \gamma_l \cos \theta,$$

Where  $\gamma_s$  and  $\gamma_{sl}$  are the solid/gas and solid/liquid interfacial tensions, respectively,  $\gamma_l$  is the liquid/gas surface tension, and  $\theta$  is the contact angle.

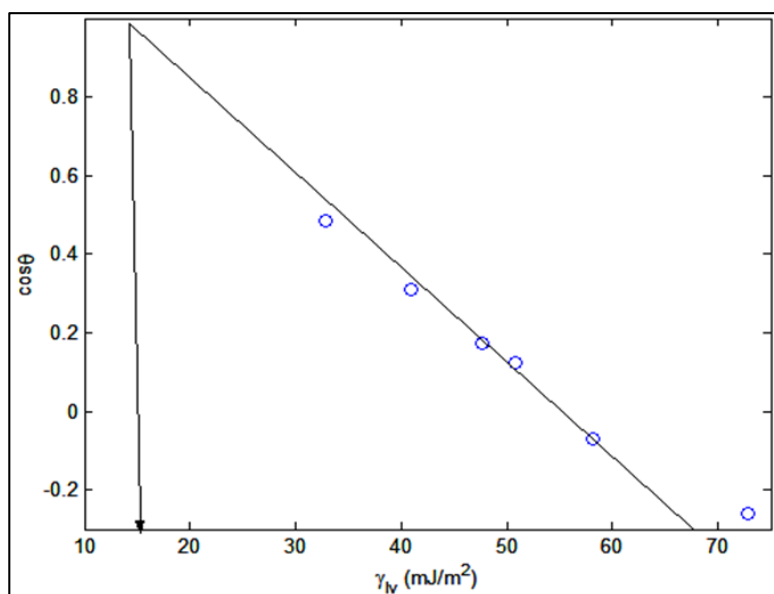
Interfacial theories, together with Young's equation, are used not only to calculate the solid surface tension, but also the characterization profile and the work of adhesion of the solid surface. It is especially used for the identification of the contaminants present for the possible modification of the surface and in study of adhesion.



**Fig 6:** Zisman plot of 17-propylene with the data from liquids 1-7 shown in table 3



**Fig 7:** Zisman plot of Paraffin with the data from liquids 1-4 shown in table 3



**Fig 8:** Zisman plot of 17-ethylene with the data from liquids 1-6 shown in table 3



Since the solid surface tension of a given solid surface is expected to be constant i.e., independent of the choice of the testing liquid used.

The critical surface tension is obtained by simply reading the value of the surface tension (on the x-axis) for which the cosine of the contact angle is 1 (i.e., when the contact angle is 0). It is approximately equal to 18.23 MJ/m<sup>2</sup> for 17-(Perfluoropropyl)-heptadecanoic, 21.77MJ/m<sup>2</sup> for paraffin and 16.65MJ/m<sup>2</sup> for 17-(Perfluoropropyl)-heptadecanoic acid. 17-(Perfluoropropyl)-heptadecanoic is the easiest surface to weight as it has the highest critical surface tension among the three solid surfaces. The work of adhesion can be calculated from the Young-Dupre equation,  $W_{adh} = \gamma_{lv}(1 + \cos \theta)$  as both the surface tension of the liquid and the contact angles are available.

For water, the work of adhesion as calculated from Young and Dupre equation for solid surfaces FC-722-coated mica, FC-725-coated silicon water, and Poly (methyl methacrylate) (Data from ADSA-P technique) respectively are 37.7988, 37.1108, 93.0801. When the Goniometric data were treated the work of adhesion by Young and Dupre equation yields 92.7336, 50.3035, 53.9579 for solid surfaces: 17-(perfluoropropyl)-heptadecanoic acid, Paraffin, and 17-(perfluoroethyl)-heptadecanoic respectively. Use the Zisman plot is very useful in wetting studies. There are, however, some complications with the Zisman plot. First, it is recommended to construct the Zisman plot with pure liquids. Mixtures or surfactants solutions may alter the solid surface due to adsorption. Moreover, the choice of test liquids used to construct the Zisman plot is observed to affect the results, and critical surface tensions may be obtained depending upon whether polar, non-polar or hydrogen-bonding fluids are used.

### Conclusion

The equation of state of Bertholet (modified), the new equation of state of Bertholet (modified with alternative formulation) and the equation of state of Neumann are found superior than that of the Young's equation in predicting the solid-vapour interfacial tension for any combination of solid surface and vapour-liquid interfacial tension, and with the known values of the contact angle and liquid interfacial tension. The work also justifies the method of Zisman for calculating solid-vapour interfacial tension. The work of adhesion can easily be calculated if the interfacial tensions are known exactly. So, more experiments need to perform in this regard in the future.

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