The Usefulness of the Equation of State for Interfacial Tensions Estimation in Some Liquid–Liquid and Solid–Liquid Systems

B. Jańczuk,*,1,2 J. M. Bruque,* M. L. González-Martín,* J. Moreno del Pozo,†
A. Zdziennicka,‡ and F. Quintana-Gragera¶

*Departamento de Física, and ¶Departamento de Matemática, Universidad de Extremadura, 06071 Badajoz, Spain; †Departamento de Informática, Universidad de Extremadura, 10004 Cáceres, Spain; and ‡Department of Physical Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Poland

Using the values of water–apolar liquid, glycerol–apolar liquid, formamide–apolar liquid, and ethylene glycol–apolar liquid surface or interfacial tension taken from the literature, the relationships between ϕ parameter of interfacial interactions and interfacial tensions were determined both graphically and mathematically. Next, the so-called "α" and "β" values obtained in this way were used for the solution of the equation of state for interfacial tensions for liquid–liquid and polymer–liquid systems. The results obtained from the calculations have shown that the α and β values are not constant, but depend on the kind of polar–apolar liquid system and the way the values are determined. The values of α and β differ from 0.0075 and 1, respectively. It has been found that it is impossible to predict the interfacial tensions of polar–apolar liquids as well as polymer–liquid systems with good accuracy on the basis of $\alpha = 0.0075$ and $\beta = 1$, and α and β values have also been determined from polar–apolar liquid interfacial tensions. © 1996 Academic Press, Inc.

Key Words: interfacial tension; parameter of interfacial interactions; contact angle; equation of state for interfacial tension.

INTRODUCTION

The equation of state approach for interfacial tensions, originated by Neumann and co-workers (1–3), is based on macroscopic thermodynamics. This equation can be formulated from contact angle data on low-energy solids. Ward and Neumann (4) assumed a solid in contact with a fluid to be ideal. The surface of the solid is smooth, homogeneous, and rigid (or nondeformable), and the solid should have no appreciative vapor pressure.

In the solid–liquid–vapor system, there is neither dissolution of the solid nor absorption by the solid of any of the components of the liquid or gaseous phases. Assuming this,

they proposed the solid–liquid interfacial tension to be a unique function of the liquid and solid surface tension (4),

$$\gamma_{ij} = f(\gamma_i, \gamma_j),\qquad [1]$$

where γ is the surface or interfacial tension, and the subscripts i and j refer to solid and liquid, respectively.

It was stated by Lee (5) that thermodynamics, by its nature, ignores the question of whether one of the phases is a solid, so Eq. [1], in principle, must apply equally to liquid–liquid and liquid–solid interfaces.

Eq. [1] can be solved, among other ways, by using the interfacial interaction parameter of Girifalco and Good (6), ϕ:

$$\gamma_{ij} = \gamma_i + \gamma_j - 2\phi(\gamma_i\gamma_j)^{1/2}.\qquad [2]$$

Neumann *et al.* (7), applying the contact angle data obtained by Zismann and co-workers (8–11) for several liquids on the surface of eight solids, pointed out that a linear relationship existed between solid–liquid interfacial tensions and ϕ,

$$\phi = -\alpha\gamma_{ij} + \beta,\qquad [3]$$

where α and β are empirical constants.

The values of α and β are equal to 0.0075 and 1, respectively (4, 7).

Thus, the purpose of our paper is to use these values to predict liquid–liquid and solid–liquid interface tension for some systems and to predict the wettability of PTFE and PET. Also, new values of α and β were estimated.

CALCULATIONS AND DISCUSSIONS

Using Eq. [3] it is possible to estimate the values of α and β from liquid–liquid interfacial tension measurements. Taking from the literature the values of γ_i, γ_j and γ_{ij} for
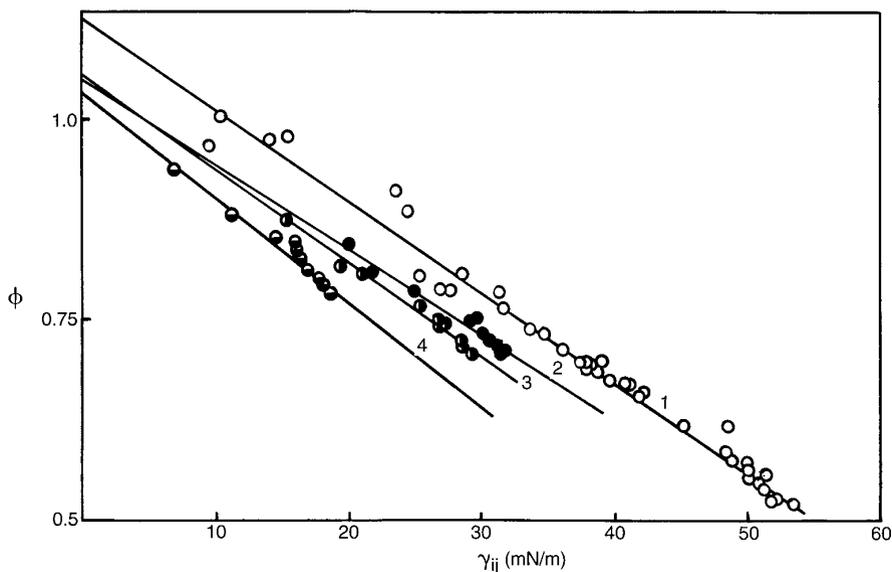

FIG. 1. The relationship between parameter ϕ and γ_{ij} (interfacial tension) for water–organic liquid (curve 1), glycerol–organic liquid (curve 2), formamide–organic liquid (curve 3), and ethylene glycol–organic liquid (curve 4) systems.

water–organic liquid, glycerol–organic liquid, formamide–organic liquid, and ethylene glycol–organic liquid systems (12, 13), the ϕ values were calculated from Eq. [2]. Next, the values of α and β were determined by plotting the relationship between ϕ and γ_{ij} (Fig. 1), which are presented in Table 1.

From Table 1 it appears that for each system studied different values of α and β were obtained. However, it must be stressed that in all cases a good rectilinear relationship between ϕ and γ_{ij} was obtained (Fig. 1 and Table 1), which is confirmed by the values of the correlation coefficient and curve-fit standard error (Table 1). Both the α and the β values obtained from liquid–liquid interfacial tensions are larger than those proposed by Neumann and co-workers (4, 7).

To clarify the reason for the differences between the α

and β values of Neumann and co-workers and those obtained from liquid–liquid interfacial tension data, Eq. [2] should be rewritten in the form

$$\phi = -\frac{1}{2(\gamma_i \gamma_j)^{1/2}} \gamma_{ij} + \frac{\gamma_i + \gamma_j}{2(\gamma_i \gamma_j)^{1/2}}. \qquad [4]$$

From Eq. [4] it results that for each pair of γ_i and γ_j we should have different values of α and β. For $\gamma_i \neq \gamma_j$, $\beta > 1$, and for $\gamma_i = \gamma_j$, $\beta = 1$. However, for many systems of $i - j$, where γ_i differs slightly from γ_j it is possible to approximate the parameter ϕ with good accuracy by one pair of α and β values, as is seen in Fig. 1 and Table 1. There is no justification for the conclusion that the α and β values are 0.0075 and 1, respectively. Assuming, however,

TABLE 1

Values of α and β for Water–Organic Liquid, Glycerol–Organic Liquid, Formamide–Organic Liquid, and Ethylene Glycol–Organic Liquid Systems Determined from Fig. 1 (No. 1) and from Eq. [5] (No. 2) (the Average Values of α), with Correlation Coefficients (cc) and Curve-Fit Standard Errors (cfse)

Liquid	No.	α	β	cc	cfse
Water	1	0.01133 ± 0.00018	1.129 ± 0.007	0.9919	0.01698
	2	0.00768 ± 0.00197	1.000		
Glycerol	1	0.01049 ± 0.00069	1.050 ± 0.020	0.9750	0.00954
	2	0.00873 ± 0.00043	1.000		
Formamide	1	0.01153 ± 0.00052	1.052 ± 0.014	0.9880	0.00777
	2	0.00946 ± 0.00052	1.000		
Ethylene glycol	1	0.01291 ± 0.00078	1.032 ± 0.013	0.9789	0.00906
	2	0.01095 ± 0.00088	1.000		

after Neumann and co-workers (4, 7) that these α and β values give the best approximation of the parameter ϕ, Eqs. [2] and [3] should be compatible. For $\beta = 1$, from Eqs. [2] and [3], results

$$\alpha = \frac{1}{2(\gamma_i \gamma_j)^{1/2}} - \frac{\gamma_i + \gamma_j}{2\gamma_{ij}(\gamma_i \gamma_j)^{1/2}} + \frac{1}{\gamma_{ij}} . \qquad [5]$$

If the approach of Neumann and co-workers (4, 7) is really valid for $i - j$ systems we should obtain from Eq. [5] α values close to 0.0075. Introducing into this equation the values of γ_i, γ_j, and γ_{ij} taken from the literature (12, 13), the α values were calculated for the systems water–organic liquid, glycerol–organic liquid, formamide–organic liquid, and ethylene glycol–organic liquid. The values of α for each system studied are presented in Tables 2–5, and the average values in Table 1.

From Table 2 it appears that for water–organic liquid systems including aliphatic hydrocarbons the α values range from 0.00857 (water–2-methylbutane) to 0.00895 (water–decane). Slightly smaller values of α are observed for water–aromatic hydrocarbon systems (0.0077–0.00828) (water–benzene and water–n-butylbenzene). For water–aromatic chloride systems the α values are close to those for water–aromatic hydrocarbon systems. In the case of water–aliphatic chloride systems a wide scattering of α values is evident, ranging from 0.00143 for water–isoamyl chloride to 0.00845 for water–carbon tetrachloride. For water–aromatic nitrocompound systems the α values are close to those for the water–benzene system. However, the smallest α values are obtained for water–nitrilocompound systems. In the case of water–butyronitrile system the α value calculated from Eq. [5] is smaller than 0.

It is worth noticing that the average value of α for water–organic liquid systems is equal to 0.00768 (Table 1), and this value is close to that determined by Neumann *et al.* (7) from contact angle data (0.0075).

In the case of glycerol–apolar liquid, formamide–apolar liquid, and ethylene glycol–apolar liquid systems only 14 apolar liquids are considered: 11 n-alkanes, benzene, α-bromonaphthalene, and diiodomethane (Table 3–5). From Tables 3–5 it results that the α values increase in the series of n-alkanes from n-hexane to n-hexadecane. These values differ considerably from those obtained for polar liquid–benzene, polar liquid–α-bromonaphtalene, and polar liquid–diiodomethane systems. For these systems we can state that for a given apolar liquid the α values increase as the surface tension of polar liquid decreases (from water to ethylene glycol) (Tables 2–5). On the other hand, when the differences between γ_i and γ_j for polar and apolar liquid decrease, an increase of α values is evident.

The average α values (Table 1) increase with decreased surface tension of polar liquids; e.g., in the series water, glycerol, formamide, and ethylene glycol. We can generally say that for most cases the α values calculated from Eq. [5] on the basis of interfacial tensions of polar–apolar liquid systems are considerably higher than 0.0075.

For water–hydrocarbon systems the α value does not depend on the kind of hydrocarbon, in contrast to other polar liquid–hydrocarbon systems. The dependence may be caused, in the case of organic polar liquids, by the specific orientation of hydrocarbon molecules at the hydrocarbon–polar liquid interface (14, 15).

It is characteristic that for polar–apolar liquid systems including apolar liquids which can interact with polar liquids by weak acid–base forces, the α values are closer to those determined by Neumann and co-workers (4, 7) than the other α values (Tables 2–5). Very small values of α for some hydrocarbon chlorides and nitrilocompounds can be probably caused by high solubility of these liquids in water as well as by the possibility of some chemical reactions at the water–organic liquid interface (12).

To show the usefulness of the α and β values listed in Table 1 for prediction of interfacial tensions for water–apolar liquid, glycerol–apolar liquid, formamide–apolar liquid, and ethylene glycol–apolar liquid systems, the values of γ_{ij} for these systems were calculated from the following equation (4, 7):

$$\gamma_{ij} = \frac{\gamma_i + \gamma_j - 2\beta(\gamma_i \gamma_j)^{1/2}}{1 - 2\alpha(\gamma_i \gamma_j)^{1/2}} . \qquad [6]$$

The γ_{ij} values determined are presented in Tables 2–5. In these tables, in column ''1'' the γ_{ij} values taken from the literature (12, 13) are listed, in column ''2'' γ_{ij} calculated from Eq. [6] on the basis of α and β values obtained from Fig. 1, in column ''3'' the γ_{ij} values determined from Eq. [6] using α values from Tables 2–5 and $\beta = 1$, and in column ''4'' the γ_{ij} values calculated for Neumann's (4, 7) values of α and β (0.0075 and 1, respectively). In Tables 2–5 there are also presented the values of average deviations for a given polar liquid between the measured and calculated values of γ_{ij} in three groups of systems: (1) for polar liquid–hydrocarbon (interacting across interface only by dispersion forces), (2) for polar liquid–other apolar liquid (interacting also by weak acid–base forces), and (3) for all polar liquid–apolar liquid systems.

From Tables 2–5 it appears that for most liquids any pair of α and β values is not proper to predict interfacial polar–apolar liquid tensions. In some cases the error is higher than 100%. Of course, for α and β values determined graphically minimal total average values of deviations between the measured and calculated γ_{ij} values are observed. The worst results are evident for $\alpha = 0.0075$ and $\beta = 1$. However, in

TABLE 2

Values of α for Water–Organic Liquid System Calculated from Eq. [5], Measured Values of Interfacial Tension for This System Taken from the Literature (γ_{ij}—Column 1) (12), and Values of Water–Organic Liquid Interfacial Tension Calculated from Eq. [6] Using α and β Values Obtained from Fig. 1 (γ_{ij}—Column 2), α Values Determined from Eq. [5] and $\beta = 1$ (γ_{ij}—Column 3), and Neumann's (4, 7) Values of α and β (γ_{ij}—Column 4)

Liquid	α (Eq. [5])	γ_{ij}			
		1	2	3	4
n-Hexane	0.00880	50.70	50.4	41.4	40.3
n-Heptane	0.00888	51.20	49.3	40.1	38.8
n-Octane	0.00891	51.50	48.1	38.7	37.4
n-Decane	0.00893	52.00	46.3	37.2	35.8
n-Dodecane	0.00895	52.80	44.0	36.1	34.6
n-Tetradecane	0.00891	52.20	42.5	35.8	34.2
n-Hexadecane	0.00891	53.30	54.9	34.7	33.0
2-Methylbutane	0.00857	50.10	52.5	44.1	43.1
2,2-Dimethylbutane	0.00861	49.70	51.7	43.0	41.9
2,3-Dimethylbutane	0.00868	49.80	50.8	41.9	40.8
2-Methylpentane	0.00863	48.90	50.2	41.1	39.9
3-Methylpentane	0.00872	49.90	50.4	41.4	40.2
3-Ethylpentane	0.00883	50.50	49.0	39.7	38.4
2,4-Dimethylpentane	0.00873	50.00	50.4	41.3	40.2
3-Methylhexane	0.00881	50.40	49.4	40.2	38.9
3-Ethylhexane	0.00886	50.80	48.0	38.6	37.3
3-Methylheptane	0.00884	50.50	48.2	38.8	37.5
2-Methyl-3-ethylheptane	0.00882	50.20	48.0	38.6	37.3
2,2,4-Trimethylpentane	0.00876	50.00	49.9	40.7	39.5
Cyclohexane	0.00880	50.20	42.9	35.9	34.3
cis-Decalin	0.00868	51.24	44.5	31.9	29.8
trans-Decalin	0.00873	50.70	46.2	33.1	31.3
Benzene	0.00770	33.90	47.4	33.7	31.9
Toluene	0.00787	36.10	48.1	34.0	32.2
o-Xylene	0.00794	36.10	46.0	33.0	31.2
m-Xylene	0.00804	37.90	47.4	33.7	31.9
Mesitylene	0.00809	38.70	47.6	33.8	32.0
p-Cymene	0.00772	34.60	49.2	34.2	32.5
Ethylbenzene	0.00808	38.40	47.0	33.5	31.7
n-Propylbenzene	0.00816	39.60	47.3	33.7	31.9
n-Butylbenzene	0.00828	41.40	47.0	33.5	31.7
Carbon tetrachloride	0.00849	45.00	70.9	34.9	33.3
Bromoform	0.00813	40.90	39.9	28.1	24.9
Diiodomethane	0.00789	48.50	36.3	29.9	22.5
Chloroform	0.00732	31.60	58.3	34.8	33.1
1,1,2,2-Tetrabromoethane	0.00784	38.80	36.7	28.9	22.5
1,2,3-Tribromopropane	0.00797	38.50	38.3	27.5	23.4
Dichloromethane	0.00678	28.30	26.8	35.2	33.6
Isoamyl chloride	0.00143	15.40	46.4	37.2	35.8
Ethyl bromide	0.006928	31.20	45.6	36.7	35.2
tert-Butyl chloride	0.003844	23.75	49.4	40.1	38.9
Isobutyl chloride	0.004905	24.40	47.7	38.4	37.0
Iodobenzene	0.008192	41.80	40.7	28.6	25.7
α-Bromonaphthalene	0.008058	42.10	38.7	27.5	23.7
α-Chloronaphthalene	0.008112	40.70	39.8	28.0	24.8
Bromobenzene	0.008120	38.10	42.2	29.8	27.4
Chlorobenzene	0.008086	37.40	43.3	31.1	29.0
o-Nitrotoluene	0.007635	27.20	39.9	28.1	24.9
Nitromethane	0.003476	9.50	42.1	29.7	27.2
Nitrobenzene	0.007593	25.70	38.9	27.6	23.9
m-Nitrotoluene	0.007660	27.70	40.0	28.1	24.9
Isovaleronitrile	0.001885	14.10	40.0	35.5	33.9
Butyronitrile	−0.000044	10.40	49.2	34.2	32.5
Carbon disulfide	0.008582	48.40	44.4	31.8	29.8
Phenyl isothiocyanate	0.008078	39.00	39.9	28.1	24.9
Average deviation					
1			3.1	11.9	13.3
2			12.3	9.5	11.0
3			8.6	10.5	11.9

Note. Average deviation between the measured (column 1) and calculated (columns 2, 3, and 4) values of γ_{ij} in three groups of systems: (1) for water–hydrocarbon (interacting across interface only by dispersion forces), (2) for water–other apolar liquid (interacting also by weak acid–base forces), and (3) for all water–apolar liquid systems.

TABLE 3

Values of α for Glycerol–Organic Liquid System Calculated from Eq. [5], Measured Values of Interfacial Tension for This System Taken from Literature (γ_{ij}—column 1) (13), and Values of Glycerol–Organic Liquid Interfacial Tension Calculated from Eq. [6] Using α and β Values Obtained from Fig. 1 (γ_{ij}—Column 2), α Values Determined from Eq. [5] and $\beta = 1$ (γ_{ij}—Column 3), and Neumann's (4, 7) Values of α and β (γ_{ij}—column 4)

| Liquid | α (Eq. [5]) | γ_{ij} | | | |
		1	2	3	4
n-Hexane	0.00809	29.93	35.3	33.2	27.5
n-Heptane	0.00840	29.91	33.6	31.8	25.7
n-Octane	0.00852	29.42	32.2	30.7	24.4
n-Nonane	0.00876	30.22	31.1	30.0	23.4
n-Decane	0.00886	30.32	30.1	29.3	22.6
n-Undecane	0.00902	31.12	29.2	28.8	21.9
n-Dodecane	0.00901	30.81	28.8	28.6	21.6
n-Tridecane	0.00909	31.45	28.4	28.4	21.4
n-Tetradecane	0.00910	31.40	28.2	28.2	21.2
n-Pentadecane	0.00913	31.54	27.9	28.1	21.0
n-Hexadecane	0.00918	31.81	27.3	27.8	20.6
Benzene	0.00777	19.89	23.4	26.3	18.6
α-Bromonaphthalene	0.00870	21.78	31.9	22.6	8.0
Diiodomethane	0.00857	24.86	26.2	69.6	4.6
Average deviation					
1			2.8	2.4	7.9
2			5.0	17.2	11.8
3			3.3	5.5	8.7

Note. Average deviation between the measured (column 1) and calculated (columns 2, 3, and 4) values of γ_{ij} in three groups of systems: (1) for glycerol–hydrocarbon (interacting across interface only by dispersion forces, (2) for glycerol–other apolar liquid (interacting also by weak acid–base forces), and (3) for all glycerol–apolar liquid systems.

the case of the glycerol, formamide, and ethylene glycol-*n*-alkane systems the average deviations between the measured ($\gamma_{ij}(1)$) and calculated ($\gamma_{ij}(3)$) interfacial tensions are the smallest among all considered. We must emphasize that for water–apolar liquid systems a larger number of apolar liquids are used, including those interacting by acid–base forces across interface, than for other polar–apolar liquid systems. It is interesting that in the case of water–apolar liquid systems using the values $\alpha = 0.0075$ and $\beta = 1$ for calculation of γ_{ij} (4) from Eq. [6], the prediction is the worst if the system includes hydrocarbons in which only dispersion forces interact across the water–apolar liquid interface. Unfortunately, for other polar–apolar liquid systems, we have three cases in which acid–base interaction occurs across the interface and we cannot draw a general conclusion that in the system polar–hydrocarbon liquids the α and β values proposed by Neumann and co-workers (4, 7) give the worst results among all the systems. It is quite incomprehensible that for the systems water–aromatic hydrocarbons and also water–aromatic nitrocompounds the best agreement between the values calculated for $\alpha = 0.0075$ and $\beta = 1$ and the measured ones of γ_{ij} is evident. For such systems acid-base interactions and also some mutual solubility cannot be excluded. It is quite contrary to the

assumption made by the authors of the equation of state for interfacial tensions (4, 7) and also to the results obtained recently by other authors (5).

On the basis of the data presented in Table 2–5 we can state that, except for some systems, it is impossible to predict with good accuracy the interfacial tension for polar–apolar liquid systems using the equation of state for interfacial tensions (4, 7). It must be emphasized that a good linear relationship between ϕ and liquid–liquid interfacial tensions does not guarantee that the obtained α and β constant values in the function $\phi = -\alpha\gamma_{ij} + \beta$ can be used successively for prediction of γ_{ij} values. However, it is commonly known that Neumann and co-workers (4, 7) suggest without any thermodynamic justification that their equation of state for interfacial tensions can be used only in ideal systems, which were described above.

Therefore, we tried to test the usefulness of $\alpha = 0.0075$ and $\beta = 1$ values for prediction of PTFE and PET wettability by some liquids and also PTFE–liquid and PET–liquid interfacial tensions.

Neumann and co-workers (4, 7), using the contact angle values for many liquids measured on low-energy polymers by Zisman *et al.* (8–10), determined α and β values in Eq. [3] equal to 0.0075 and 1, respectively, as was mentioned earlier.

TABLE 4

Values of α for Formamide–Organic Liquid System Calculated from Eq. [5], Measured Values of Interfacial Tension for This System Taken from the Literature (γ_{ij}—Column 1) (13), and Values of Formamide–Organic Liquid Interfacial Tension Calculated from Eq. [6] Using α and β Values Obtained from Fig. 1 (γ_{ij}—Column 2), α Values Determined from Eq. [5] and $\beta = 1$ (γ_{ij}—Column 3), and Neumann's (4, 7) Values of α and β (γ_{ij}—Column 4)

| Liquid | α (Eq. [5]) | γ_{ij} | | | |
		1	2	3	4
n-Hexane	0.00904	27.50	32.1	29.5	22.0
n-Heptane	0.00923	26.98	30.5	28.2	20.3
n-Octane	0.00914	25.41	29.1	27.2	19.0
n-Nonane	0.00958	27.22	27.9	26.5	18.1
n-Decane	0.00968	27.36	26.9	25.9	17.2
n-Undecane	0.00968	26.92	25.9	25.4	16.6
n-Dodecane	0.00987	28.40	25.4	25.1	16.3
n-Tridecane	0.00994	28.87	25.0	25.0	16.0
n-Tetradecane	0.00997	29.14	24.7	24.8	15.9
n-Pentadecane	0.00989	28.24	24.4	24.7	15.7
n-Hexadecane	0.00995	28.70	23.5	24.4	15.3
Benzene	0.00811	15.40	17.0	23.1	13.4
α-Bromonaphthalene	0.00933	19.46	24.6	27.0	4.0
Diiodomethane	0.00906	21.02	20.9	−8.7	1.4
Average deviation					
1			3.1	2.5	10.2
2			2.3	15.0	12.4
3			2.6	5.2	10.7

Note. Average deviation between the measured (column 1) and calculated (columns 2, 3, and 4) values of γ_{ij} in three groups of systems: (1) for formamide–hydrocarbon (interacting across interface only by dispersion forces), (2) for formamide–other apolar liquid (interacting also by weak acid–base forces), and (3) for all formamide–apolar liquid systems.

Combining the Young Equation,

$$\gamma_S - \gamma_{SL} = \gamma_L \cos \theta \qquad [7]$$

(where subscripts S and L refer to solid and liquid, respectively, and θ is the contact angle), with Eq. [6], for $\beta = 1$, we obtain

$$\alpha = \frac{1}{2(\gamma_S\gamma_L)^{1/2}} - \frac{\gamma_S + \gamma_L}{2(\gamma_S - \gamma_L\cos\theta)(\gamma_S\gamma_L)^{1/2}} + \frac{1}{\gamma_S - \gamma_L\cos\theta} \qquad [8]$$

Of course α should be equal to 0.0075.

Equation [8] was tested for many PTFE–liquid and PET–liquid systems. The calculations were made in the following way: for PET–polar liquids the contact angle (Table 6) and the γ_L and γ_S values were taken from Li and Neumann's paper (5, Table 8), and for apolar liquids the γ_S value was 35.63 (the average value from (5, Table 8)), and contact angles (Table 6) and γ_L values were taken from our paper (16). In the case of PTFE–liquid systems the values of θ (Table 7) and γ_L were from our papers (16, 17) and

γ_S was from Spelt and Neumann's paper (18) ($\gamma_S = 20$ mJ/m^2).

The α values calculated in this way are presented in Table 6 and 7, respectively.

From Table 6 it appears that the α values calculated for the PET–polar liquid system are close to 0.0075; however, they decrease from 0.0077 to 0.00696 with the surface tension increase of the liquids in the series diethyl glycol, ethylene glycol, formamide, glycerol, and water. For apolar liquid systems the α values are almost two times higher than 0.0075 and, except diiodomethane, there are only slight differences among the α values for the particular liquids.

In the case of PTFE–liquid systems there are only four polar liquids (Table 7) and for these liquids the α values are higher than 0.0075 and, similarly to PET–liquid systems, decrease with the increase of liquid surface tensions. For apolar liquids there is no correlation between α and γ_L. The α values depend on the kind of the liquid and are quite different from 0.0075 and those obtained for polar liquids. For some liquids there are negative α values. In conclusion, it is evident that the α values calculated from Eq. [8] for many polymer–liquid systems are not constant, and big differences between them and 0.0075 value are observed. Taking into account these values of α and $\alpha = 0.0075$ for $\beta =$

TABLE 5

Values of α for Ethylene Glycol–Organic Liquid System Calculated from Eq. [5], Measured Values of Interfacial Tension for This System Taken from the Literature (γ_{ij}—Column 1) (13), and Values of Ethylene Glycol–Organic Liquid Interfacial Tension Calculated from Eq. [6] Using α and β Values Obtained from Fig. 1 (γ_{ij}—Column 2), α Values Determined from Eq. [5] and $\beta = 1$ (γ_{ij}—Column 3), and Neumann's (4, 7) Values of α and β (γ_{ij}—Column 4)

| Liquid | α (Eq. [5]) | γ_{ij} | | | |
		1	2	3	4
n-Hexane	0.00949	16.12	22.1	20.2	12.7
n-Heptane	0.01012	16.20	20.4	18.9	11.2
n-Octane	0.01059	16.51	18.9	17.8	10.1
n-Nonane	0.01095	17.06	17.7	17.1	9.3
n-Decane	0.01104	16.85	16.5	16.4	8.6
n-Undecane	0.01130	17.69	15.4	15.9	8.1
n-Dodecane	0.01137	17.88	14.8	15.7	7.8
n-Tridecane	0.01144	18.16	14.3	15.5	7.6
n-Tetradecane	0.01145	18.12	13.9	15.4	7.5
n-Pentadecane	0.01149	18.30	13.5	15.3	7.4
n-Hexadecane	0.01155	18.52	12.4	14.9	7.0
Benzene	0.00872	7.04	1.8	13.5	5.6
α-Bromonaphthalene	0.01072	11.16	14.7	−4.5	0.2
Diiodomethane	0.010081	14.44	11.3	−0.4	0.1
Average deviation					
1			3.5	2.2	8.6
2			4.0	12.3	8.9
3			3.6	4.4	8.6

Note. Average deviation between the measured (column 1) and calculated (columns 2, 3, and 4) values of γ_{ij} in three groups of systems: (1) for ethylene glycol–hydrocarbon (interacting across interface only by dispersion forces), (2) for ethylene glycol–other apolar liquid (interacting also by weak acid–base forces), and (3) for all ethylene glycol–apolar liquid systems.

TABLE 6

Values of Contact Angle on PET Taken from Ref. (3) ($\theta_d(1)$) and Refs. (16, 17) ($\theta_d(2)$), Calculated from Eq. [7] (θ_c), Values of α for PET–Liquid System Calculated from Eq. [8], and Values of PET–Liquid Interfacial Tension (γ_{ij}) Calculated from Eq. [6] for α Determined from Eq. [8] and $\beta = 1$ (Column 1) and for $\alpha = 0.0075$ and $\beta = 1$ (4, 7) (Column 2)

| Liquid | θ_d (1) | θ_d (2) | θ_c | α (Eq. [8]) | γ_{ij} | |
					1	2
Diethyl glycol	41.19	—	41.08	0.007702	1.5	1.5
Ethylene glycol	47.52	51.1	47.45	0.007628	2.7	2.7
Thiodiglycol	55.57	—	55.67	0.007448	5.4	5.5
Formamide	61.50	63.1	61.77	0.007392	8.0	8.2
Glycerol	68.10	68.3	69.17	0.007229	12.3	13.4
Water	79.09	76.5	83.29	0.006963	22.3	27.5
Bromoform		21.4	32.24	0.01397	−3.0	0.5
Diiodomethane		40.8	51.07	0.01733	−2.8	3.7
1,1,2,2-Tetrabromoethane		37.8	49.22	0.01569	−3.6	3.2
1,2,3-Tribromoethane		26.1	41.24	0.01386	−5.2	1.5
Iodobenzene		19.2	26.98	0.01408	−1.9	0.3
α-Bromonaphthalene		22.7	39.57	0.01369	−5.5	1.3
α-Chloronaphthalene		18.5	33.02	0.01375	−4.6	0.6
Bromobenzene		14.8	12.61	0.01365	0.3	0.01
Nitromethane		30.0	14.62	0.01377	3.4	0.02
Nitrobenzene		11.8	38.05	0.01338	−7.4	1.1
Phenyl isothiocyanate		18.0	32.24	0.01376	−3.8	0.5

TABLE 7
Values of Contact Angle Taken from the Literature (16, 17) (θ_d) and Calculated from Eq. (7) (θ_c), Values of α for the PTFE–Liquid System Calculated from Eq. [8], and Values of Interfacial Tension for This System Calculated from Eq. [6] for α Determined from Eq. [8] and $\beta = 1$ (Column 1) and for $\alpha = 0.0075$ and $\beta = 1$ (4, 7) (Column 2)

Liquid	θ_d	θ_c	α (Eq. [8])	γ_{ij} 1	γ_{ij} 2
Ethylene glycol	89.0	79.5	0.01106	19.2	11.3
Formamide	102.7	89.7	0.01038	32.7	19.7
Glycerol	104.8	95.3	0.00938	36.2	25.8
Water	111.0	104.7	0.00842	46.0	38.5
Benzene	45.6	49.6	0.10284	−0.2	1.3
Toluene	43.1	48.6	0.04036	−0.8	1.2
o-Xylene	48.2	52.4	0.35508	−0.1	1.6
m-Xylene	42.7	49.6	0.03451	−1.2	1.3
Mesitylene	48.1	49.4	−0.00091	0.8	1.3
p-Cymene	44.5	47.6	0.36329	−0.04	1.1
Ethylbenzene	44.6	50.3	0.04338	−0.8	1.4
n-Propylbenzene	43.9	49.8	0.04020	−0.9	1.3
n-Butylbenzene	43.4	50.4	0.03526	−1.2	1.4
Carbon tetrachloride	33.2	44.5	0.02590	−2.5	0.8
Bromoform	62.9	71.5	−0.04416	1.1	6.8
Diiodomethane	72.0	82.7	−0.01002	4.3	13.5
Chloroform	37.3	45.1	0.02878	−1.6	0.8
1,1,2,2-Tetrabromoethane	76.3	81.4	0.00305	8.2	12.6
1,2,3-Tribromopropane	70.5	76.5	−0.00099	4.8	9.4
Dichloromethane	46.5	43.2	0.01608	1.8	0.7
Isoamyl chloride	63.1	32.6	0.02272	9.5	0.2
Ethyl bromide	37.3	35.5	0.01666	0.8	0.3
tert-Butyl chloride	34.1	—	0.02524	3.7	0.0
Isobutyl chloride	37.0	24.4	0.02348	2.5	0.06
Iodobenzene	64.2	69.0	−0.00406	2.7	5.8
α-Bromonaphthalene	66.0	75.5	−0.02708	1.9	8.8
α-Chloronaphthalene	64.4	71.9	−0.01814	1.9	7.0
Bromobenzene	58.1	64.2	−0.04551	0.7	4.1
Chlorobenzene	52.8	59.3	0.12685	−0.3	2.9
o-Nitrotoluene	64.2	71.5	−0.01740	1.9	6.8
Nitromethane	75.1	64.7	0.01398	10.5	4.3
Nitrobenzene	69.4	74.6	−0.00031	4.5	8.4
m-Nitrotoluene	66.4	71.4	−0.00215	3.4	6.8
Isovaleronitrile	67.0	41.7	0.02105	9.8	0.6
Butyronitrile	79.2	47.6	0.02011	14.8	1.1
Carbon disulfide	51.7	56.9	1.54957	−0.02	2.4
Phenyl isothiocyanate	65.0	71.5	−0.01001	2.5	6.8

1 from Eq. [6] the γ_{SL} values were calculated and listed in Tables 6 and 7 in the columns denoted ''1'' and ''2,'' respectively. It is seen from Tables 6 and 7 that there are differences between $\gamma_{SL}(1)$ and $\gamma_{SL}(2)$ even for PET–polar liquid systems for which the α values calculated from Eq. [6] are close to 0.0075 (particularly for water). In many cases the $\gamma_{SL}(1)$ values are negative for polymer–apolar liquid systems. Of course, we must remember that $\gamma_{SL}(1)$ values can also be obtained from the equation $\gamma_{SL} = \gamma_S - \gamma_L \cos \theta$ by using the same values of the contact angle, γ_L, and γ_S as in Eq. [8]. However, the question arises about the reason of this kind of values and the differences between $\gamma_{SL}(1)$ and $\gamma_{SL}(2)$.

Contact angle measurements are the source of many errors that are often overlooked. As the subtleties involved are not appreciated, many investigations have been misled by inaccurate data. Li and Neumann (3) suggest that for this reason the equation of state for interfacial tensions is not valid for many systems because the values of the contact angle are not properly measured.

Now we try to calculate the contact angle using the Young equation and γ_{SL} values determined for $\alpha = 0.0075$ and $\beta = 1$.

The θ_c values calculated from Eq. [7] in this way are shown in Tables 6 and 7 together with the measured values taken from the literature (3, 16, 17). The contact angle

$\theta_d(1)$ in Table 6 is from paper (3) and $\theta_d(2)$ is from papers (16, 17).

From Table 6 it appears that the contact angles measured by us (17) for ethylene glycol, formamide, glycerol, and water on PET differ only slightly from those determined ''very exactly'' by Li and Neumann (3). This means that PET surface used in two different laboratories has the same properties. For polar liquids there are small differences between the values of the measured and calculated contact angles. In the case of apolar liquids the calculated values for a given liquid, except bromobenzene and nitromethane, are considerably higher than those measured. Spelt and Neumann (18) suggest that the advancing contact angle, measured improperly, can be smaller by 7° than its ''true'' value. However, in many cases, the differences between measured and calculated contact angles are bigger by 10° or more. This suggests that not the procedure of contact angle measurements is wrong but α values are not constant for many systems. We must remember that for calculations we consequently take the surface tension values for PET determined by Li and Neumann (3), which are considerably smaller than those determined by other researchers. (See Ref. in (16)).

Differences between calculated (θ_c) and measured (θ_d) contact angles are also observed for PTFE-liquid systems (Table 7).

It is interesting that for all four polar liquids the measured values are bigger than those calculated. For many apolar liquids the differences between θ_d and θ_c are not larger than 4°, but the differences between the α values calculated from Eq. [7] and Neumann's values are considerable. For example, for benzene α calculated from Eq. [7] is 0.10028, many times bigger than 0.0075, but the difference between θ_d and θ_c is only 4°. This means that the value 0.0075 has varying sensitivity depending on γ_S and γ_L values.

Of course, as can be seen from Eq. [6], the denominator of this equation may become zero for certain surface tensions. To avoid the problem of discontinuity of Eq. [6], Li and Neumann have recently expressed this equation in a new form (19),

$$\gamma_{ij} = \gamma_i + \gamma_j - 2(\gamma_i\gamma_j)^{1/2}e^{-b(\gamma_i - \gamma_j)^2}, \qquad [9]$$

where b is the constant value, which was determined to equal 0.0001247 (3).

If Eqs. [6] and [9] are compatible then we can approximate them by the simplest function, for example, a polynomial, which should give nearly the same values of γ_{ij} for a given γ_i and γ_j.

Since the α and β values in Eq. [6] have been found to equal 0.0075 and 1, respectively, on the basis of contact angle measurements for a series of liquids on solid surface which surface tensions are in the range from 15 to 72 and from 10 to 40 mJ/m^2, respectively, we have made a mathematical analysis of Eqs. [6] and [9] for such a range of γ_i and γ_j values. It has appeared that Eq. [6] may be approximated by the equation

$$\gamma_{ij} = C_0 + C_1\gamma_j + C_2\gamma_j^2 + C_3\gamma_j^3 + C_4\gamma_j^4 + C_5\gamma_j^5, \quad [10]$$

where C_0, C_1, C_2, C_3, C_4, and C_5 are the constant values for a given γ_i which can be determined from

$$C_0 = -3.23823 + 2.74523 \ 10^{-1} \ \gamma_i$$
$$+ 2.22389 \ 10^{-2} \ \gamma_i^2 - 2.7938 \ 10^{-4} \ \gamma_i^3$$

$$C_1 = 2.9071 \ 10^{-1} - 7.229 \ 10^{-2} \ \gamma_i$$
$$- 6.72514 \ 10^{-5} \ \gamma_i^2 + 2.12432 \ 10^{-5} \ \gamma_i^3$$

$$C_2 = 2.45351 \ 10^{-2} + 1.61134 \ 10^{-5} \ \gamma_i$$
$$+ 5.89799 \ 10^{-5} \ \gamma_i - 1.57999 \ 10^{-6} \ \gamma_i^3$$

$$C_3 = -5.1466 \ 10^{-4} + 3.43563 \ 10^{-5} \ \gamma_i$$
$$- 2.63848 \ 10^{-6} \ \gamma_i^2 + 5.3748 \ 10^{-8} \ \gamma_i^3$$

$$C_4 = 6.10294 \ 10^{-6} - 6.01609 \ 10^{-7} \ \gamma_i$$
$$+ 4.1617 \ 10^{-8} \ \gamma_i^2 - 8.20664 \ 10^{-10} \ \gamma_i^3$$

$$C_5 = -2.88569 \ 10^{-8} + 3.4232 \ 10^{-9} \ \gamma_i$$
$$- 2.24306 \ 10^{-10} \ \gamma_i^2 + 4.53008 \ 10^{-12} \ \gamma_i^3.$$

However, the best approximation of Eq. [9] can be obtained by the equation

$$\gamma_{ij} = D_0 + D_1\gamma_j + D_2\gamma_j^2 + D_3\gamma_j^3 + D_4\gamma_j^4 + D_5\gamma_j^5, \quad [11]$$

where D_0, D_1, D_2, D_3, D_4, and D_5 are the constant values for a given γ_i value which can be determined from:

$$D_0 = -3.90648 + 3.96885 \ 10^{-1} \ \gamma_i$$
$$+ 1.12986 \ 10^{-2} \ \gamma_i^2 - 6.85861 \ 10^{-5} \ \gamma_i^3$$

$$D_1 = 4.34509 \ 10^{-1} - 9.13713 \ 10^{-2} \ \gamma_i$$
$$+ 1.4611 \ 10^{-3} \ \gamma_i^2 - 8.1144 \ 10^{-6} \ \gamma_i^3$$

$$D_2 = 1.16687 \ 10^{-2} + 1.55682 \ 10^{-3} \ \gamma_i$$
$$- 4.26969 \ 10^{-5} \ \gamma_i^2 + 3.22785 \ 10^{-7} \ \gamma_i^3$$

$$D_3 = -1.27123 \ 10^{-4} - 1.4016 \ 10^{-5} \ \gamma_i$$
$$+ 3.76911 \ 10^{-7} \ \gamma_i^2 - 3.7264 \ 10^{-9} \ \gamma_i^3$$

$$D_4 = 1.03136 \ 10^{-6} + 1.19818 \ 10^{-7} \ \gamma_i$$
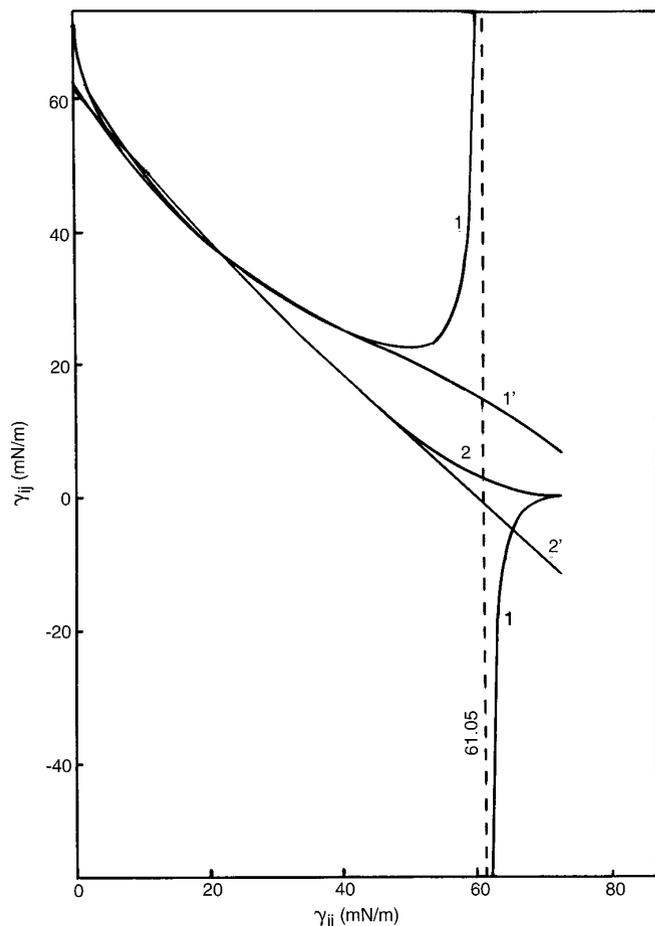$$- 1.50307 \ 10^{-9} \ \gamma_i^2 + 1.45754 \ 10^{-11} \ \gamma_i^3$$

FIG. 2. The relationship between solid–water interfacial tensions and solid surface tension. Curve 1 calculated from Eq. [6]; curve 2 calculated from Eq. [9]; curve 1′ calculated from Eq. [10]; curve 2′ calculated from Eq. [11].

$$D_5 = -4.09737 \ 10^{-9} - 5.42515 \ 10^{-10} \ \gamma_i$$
$$+ \ 3.70407 \ 10^{-12} \ \gamma_i^2 - 1.08585 \ 10^{-14} \ \gamma_i^3.$$

Comparing the values of $C_{(n)}$ and $D_{(n)}$, it results that Eq. [9] for $\beta = 0.0001247$ is not the best approximation of Eq. [6] in the range of γ_i values from 10 to 40, and γ_j values from 15 to 72 mJ/m^2. To show more clearly the differences between Eqs. [6], [9], [10], and [11] in Fig. 5, the γ_{ij} values for solid–water interface tensions in the γ_i range from 0 to 72.8 mJ/m^2 calculated from these equations are plotted as an example.

Of course, in the γ_i range from 10 to 40 mJ/m^2 Eq. [10] gives the same values of γ_{ij} as Eq. [6], and Eq. [11] as Eq. [9]. However, some differences between the γ_{ij} values obtained from Eqs. [6] and [9] are evident. In the γ_i range from 50 to 72.8 mJ/m^2 each equation gives different values of γ_{ij}. Thus it should be stressed that Eq. [9] has a quite different nature than Eq. [6] and they give similar results only in a certain range of γ_i and γ_j values. Of course, Eq. [9] cannot be used for prediction of liquid–liquid tensions, because, as results from Table 2 and Fig. 2, there is no agreement between water–organic liquid interface tension and that of solid–water interfaces calculated for the systems in which the solid surface tension γ_S is the same as the surface tension, γ_L, of organic liquid.

ACKNOWLEDGMENTS

REFERENCES

1. Neumann, A. W., and Sell, P., *Z. Phys. Chem. (Leipzig)* **227,** 187 (1964).
2. Driedger, O., Neumann, A. W., and Sell, P., *Kolloid Z. Z. Polym.* **201,** 52 (1986).
3. Li, D., and Neumann, A. W., *Adv. Colloid Interface Sci.* **39,** 299 (1992).
4. Ward, C. A., and Neumann, A. W., *J. Colloid Interface Sci.* **49,** 286 (1974).
5. Lee, L. H., *Langmuir* **9,** 1898 (1993).
6. Girifalco, L. A., and Good, R. J., *J. Phys. Chem.* **62,** 904 (1957).
7. Neumann, A. W., Good, R. J., Hope, C. J., and Sejpal, M., *J. Colloid Interface Sci.* **49,** 291 (1974).
8. Bernett, M. K., and Zisman, W. A., *J. Phys. Chem.* **66,** 1207 (1962).
9. Ellison, A. H., and Zisman, W. A., *J. Phys. Chem.* **58,** 503 (1954).
10. Shafrin, E. G., and Zisman, W. A., *J. Phys. Chem.* **66,** 740 (1962).
11. Fox, H. W., and Zisman, W. A., *J. Colloid Sci.* **7,** 109 (1952).
12. Good, R. J., and Elbing, E., *Ind. Eng. Chem.* **62,** 54 (1970).
13. Jańczuk, B., Wójcik, W., and Zdziennicka, A., *J. Colloid Interface Sci.* **157,** 384 (1993).
14. Untz, G., and Serpinel, J., *Chim. Phys.* **73,** 912 (1976).
15. Rayss, J., and Saint-Pierre, M., *J. Chim. Phys.* **79,** 133 (1982).
16. Jańczuk, B., and Białopiotrowicz, T., *J. Colloid Interface Sci.* **127,** 189 (1989).
17. Jańczuk, B., Białopiotrowicz, T., and Wójcik, W., *J. Colloid Interface Sci.* **127,** 59 (1989).
18. Spelt, J. K., and Neumann, A. W., *in* ''Modern Approaches to Wettability (Theory and Application)'' (E. M. Schrader and G. I. Loeb, Eds.), pp. 101–141. Plenum, New York, 1992.
19. Li, D., and Neumann, A. W., *J. Colloid Interface Sci.* **137,** 304 (1990).