Relationships of Surfactant Head Group Weight Fraction and Some Polarity Terms by Gas Chromatography

BARAKAT Y   MOSTAFA N E   IBRAHIM V   MANSOUR R

Egyptian Petroleum Research Institute   Cairo   Egypt

Abstract Polarity partition coefficient K methanol carbon number of surfactant $C_{\mathrm{MeOH\ S}}$ and methanol carbon number of surfactant head group $C_{\mathrm{MeOH\ HG}}$ are measured on six alkanolamides and five polyoxyethylenated long chain amines as stationary phases. From the measured methanol carbon numbers polarity indices IP_{S} and IP_{HG} are calculated. The determined polarity terms are plotted against the head group weight fraction f_{HG} of the investigated surfactants and several equations have been developed. The study reveals that the molecular structural gap between alkanolamides and polyoxyethylenated long chain amines diminished when HLB numbers of these surfactant classes are plotted against f_{HG} values. Consequently a general equation relating HLB and f_{HG} is obtained.

Key words   gas chromatography   alkanolamides   polyoxyethylenated amines   polarity terms   hydrophile weight fraction

It has been shown that retention indices measured on surfactant stationary phases through gas chromatography GC are particularly suitable for a quantitative characterization of surfactants accurately [1 2]. Retention index approach introduced by Kovats [3] is frequently used to examine the polarity of these surfactants [4 5]. Another more rigorous approach based on retention indices has been suggested by Rohrschneider [1 6] who developed an equation widely used in gas chromatography [1 2 7].

An analogous approach has been replaced by McReynolds [8] who has shown through a statistical analysis of the retention index matrix that only three components are necessary the polarity of surfactant stationary phase the polarity of solutes undergoing analysis and the specific interactions between solutes and stationary phases [9]. Both approaches used in the characterization of surfactant polarities by means of retention indices have been further explored and expanded [7 10].

Barakat *et al* [11] have recently introduced the so-called simulated hydrophobic tail SHT concept that permits the determination of some polarity terms of alkanolamide stationary phases and their head groups. This concept also permits the

distinction between polyoxyethylene head groups of nonionics having different hydrophobic moieties.

In the present work some polarity terms are measured on alkanolamides and polyoxyethylenated long chain amine stationary phases. Relations between the head group weight fraction of these surfactants and each of the measured polarity terms are studied. A general equation relating head group weight fraction and HLB number of these surfactants has been developed.

1   Experimental

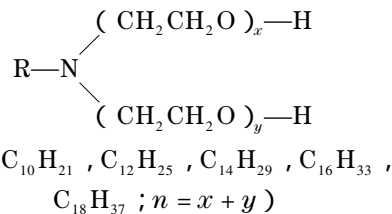### 1.1   The employed stationary phases
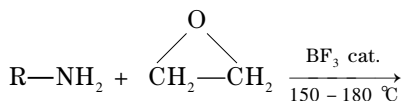
1.1.1   Alkanolamides

Alkyldiethanolamides   commercially known as alkanolamides were prepared according to the Weil Parris and Stirton method [12]. Details concerning purity were given elsewhere [11 13 14]. The prepared alkanolamides are white solids having the following general formula.
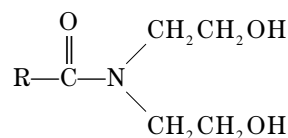
$$R = C_7H_{15}   C_8H_{17}   C_9H_{19}   C_{11}H_{23}   C_{13}H_{27}   C_{15}H_{31}$$

1.1.2 Polyoxyethylenated long chain amines

Linear long chain primary amines were ethoxylated as described previously [15 16] and purified according to Malkemus and Kilheffer methods [17 18]. The average number n of ethylene oxide EO units per alkylamine molecule was determined through nuclear magnetic resonance NMR analysis [15 19] using 60 MHz Varian spectrometer. The chemical equation is as follows.

$$R\text{—}NH_2 + \overset{O}{\overset{\diagup\diagdown}{CH_2\text{—}CH_2}} \xrightarrow[150-180\ ℃]{BF_3\ cat.}$$

$$R\text{—}N\begin{cases} CH_2CH_2O_x\text{—}H \\ CH_2CH_2O_y\text{—}H \end{cases}$$

$$R = C_{10}H_{21} \quad C_{12}H_{25} \quad C_{14}H_{29} \quad C_{16}H_{33}$$
$$C_{18}H_{37} \quad n = x + y$$

1.2 Thermal stabilities and GC applications

Thermal stabilities of the employed stationary phases surfactants were examined through thermogravimetric analysis TGA and differential thermal analysis DTA. The results are given in Table 1.

Table 1 Characteristics of the employed stationary phases

Stationary phases	Class	Physical form at 25 ℃	Maximum operating temperature/℃	Chromatographic application
Alkanolamides	nonionic	solids	130 – 150	gas-solid GSC
Polyoxyethylenated long chain amines	nonionic	liquids	120 – 140	gas-liquid GLC

1.3 GC columns and operating conditions

Stainless steel columns having equal dimensions 2 m length 6 mm o. d. and 3.5 mm i. d. were used in all measurements which were accomplished by means of a Sigma-3B Perkin Elmer chromatograph. Each column was packed with 15% stationary phase on 100 – 120 mesh acid washed Chromosorb-P. Packed columns were conditioned at 120 ℃ in N_2 carrier gas flow rate 10 – 15 mL/min. for about 3 h before use. All measurements were carried out at 110 ℃ column temperature 200 and 250 ℃ for flame ionization detector FID and injector temperatures respectively.

Two categories of stationary phases were employed polar and nonpolar. The polar ones involved the prepared surfactants i. e. alkanolamides and polyoxyethylenated long chain amines. The nonpolar stationary phases were n-alkanes purity > 95% Aldrich having a number of carbon atoms equal to that of surfactants hydrophobic tails. These nonpolar stationary phases are SHT models. More details concerning SHT models were given in reference 11.

1.4 Hydrophile-lipophile balance HLB

The HLB numbers were calculated from the well-known Griffin's equations [20] Equation 1 and Equation 2 for polyoxyethylenated long chain amines and alkanolamides [11] respectively

$$HLB = \%\ EO/5 \qquad\qquad 1$$

$$HLB = 20 \times \frac{M_H}{M_H + M_L} \qquad\qquad 2$$

M_H is molar weight of hydrophilic group and M_L is molar weight of hydrophobic group.

Equation 3 [21] which involves summation of the effects of the molecule's component groups and Equation 4 [22] relating the partition coefficient K and HLB were used to calculate HLB numbers of alkanolamides.

$$HLB = 7 + \sum \text{ hydrophilic group numbers} +$$
$$\sum \text{ hydrophobic group numbers} \qquad 3$$
$$HLB = 26 - K/2.6 \qquad\qquad 4$$

1.5 Partition coefficient

The partition coefficients of diisobutylene K_{DIB} and iso-octane K_{IO} and ethanol K_{EtOH} for the investigated surfactants were calculated from the retention times and flow rates according to the following equation [23].

$$K = \frac{3}{2} \frac{P_i/P_0{}^2 - 1}{P_i/P_0{}^3 - 1} Ft_r'/V_L \qquad 5$$

where K is the partition coefficient of the eluent P_i is the inlet pressure of carrier gas Pa P_0 is the outlet pressure of carrier gas Pa F is the flow rate of carrier gas mL/min t_r' is the corrected retention time of eluent relative to methane min V_L is the volume of stationary phase at column temperature.

For simplicity it has been assumed that 1 g surfactant equals 1 mL [24].

BARAKAT Y *et al*　Relationships of Surfactant Head Group Weight Fraction
and Some Polarity Terms by Gas Chromatography
4
· 343·

1.6　Head group weight fraction f_{HG}

f_{HG} is the ratio of formula weight of hydrophilic portion to molecular weight of surfactant.

1.7　Polarity

Absolute P_a　and relative P_r　polarities of the employed surfactant stationary phases were determined from the following relations [4,5]

$$P_a = \frac{t_{r\ EtOH}}{t_{r\ n\text{-hexane}}}$$

and

$$P_r = \frac{t_{r\ EtOH} - t_{r\ n\text{-pentane}}}{t_{r\ n\text{-hexane}} - t_{r\ n\text{-pentane}}}$$

where t_r is retention time　min.

1.8　Polarity index　IP

$C_5 - C_9$　n-alkanes　methanol and methane were injected and the relative retention volumes V'_r　of $C_5 - C_9$　n-alkanes and methanol were measured relative to the methane peak.

Polarity index of each surfactant　IP_s　is calculated from Huebner′s equation [25]　Equation 6　as described in reference　11 .

$$IP_s = 100\ \log\ \ C_{MeOH\ s}\ -4.7\ \ +60\ \ \ 6$$

where　$C_{MeOH\ s}$ is apparent methanol carbon number measurement on the employed surfactants.

Similarly　polarity index　IP_{Tail} values are calculated from Equation　7 .

$$IP_{Tail} = 100\ \log\ \ C_{MeOH\ Tail}\ -4.7\ \ +60\ \ \ \ 7$$

where　$C_{MeOH\ Tail}$ is apparent methanol carbon number measurement on SHT.

2　Results and discussion

2.1　Empirical parameters of surfactant polarity from GC measurements

The direct relation between polarity and *HLB* number of surfactant was first investigated by Becher and Birkemeir [26] who defined the polarity of a surfactant as the ratio of the retention times of polar and nonpolar material　when the surfactant acts as a stationary phase in gas chromatographic separation. The ratio of retention times was thus found to be directly proportional to the *HLB* numbers of nonionics. Because the relative parameters of polar and nonpolar solutes on the polarity characteristics of surfactant stationary phase several polarity terms have been measured through gas chromatographic methods [20-22] .

Relationships have been developed between these measured polarity terms and *HLB* numbers calculated from the surfactant molecule′s component groups or from the hydrophobic and hydrophilic formula weight [20,21] . The purpose of this work is to attempt correlation of some measured polarity terms and the head group weight fractions of surfactants of different chemical classes.

2.2　Relationships of polarity terms and f_{HG}

2.2.1　P_a-f_{HG} and P_r-f_{HG} relationships

Measured P_a and P_r values are given in Table 2. It is found that plots of P_a-f_{HG} and P_r-f_{HG} of alkanolamides and polyoxyethylenated long chain amines have a lack of linearity with considerable scatter on normal scale. These results have been reported by some investigators [27,28] who determined equations through regression analysis from relations with considerable scatter and they have obtained results with a high error of estimate. Other investigators [29] have claimed that single polarity terms　P_a or P_r　determined by gas chromatography produce a near linear relation with considerable deviation. Measurement of *IP* values permits more accurate correlations [4,5] .

The head groups of the investigated surfactants contain nitrogen atom. It has been reported [30] that retention data with considerable deviation have been obtained by using surfactants stationary phases having sulphur- and nitrogen-containing head groups. Such surfactants have been found to restrict the correlation between the

Table 2　Head group weight fraction　f_{HG}　absolute and relative polarities　P_a　P_r　and partition coefficient　K　values of the investigated alkanolamides

Stationary phases	R	Mol. Wt	f_{HG}	Polarity		Partition coefficient　K		
				P_a	P_r	diisobutylene	iso-octane	ethanol
Alkanolamides $\begin{matrix} O \\ \| \\ R—C—N \end{matrix} \begin{matrix} CH_2CH_2OH \\ \\ CH_2CH_2OH \end{matrix}$	C_7H_{15}	231	0.571	4.636	21.90	6.516	4.739	24.455
	C_8H_{17}	245	0.539	3.600	17.55	7.701	5.331	19.935
	C_9H_{19}	259	0.510	2.187	10.65	8.750	6.120	13.649
	$C_{11}H_{23}$	291	0.454	1.533	6.30	9.800	7.605	6.517
	$C_{13}H_{27}$	323	0.409	1.305	2.55	10.480	8.886	6.220
	$C_{15}H_{31}$	355	0.372	1.157	1.43	11.785	9.821	5.924

weight fraction group and retention behaviour.

Due to the lack of linearity of P_a-f_{HG} and P_r-f_{HG} plots on a normal scale an attempted semi-logarithmic plots are made and satisfactory correlations are obtained in Fig. 1. It has been reported that lack of linearity in such correlations is evident with increasing hydrophobic character in the surfactant molecule [30]. Correlations between polarity measured through GC and hydrophilic portion of surfactant molecule have shown such unrealistic scatter of data points [25,31]. These correlations have reached linearity by using the logarithms of the measured polarities P_a and P_r and retention volumes [30].
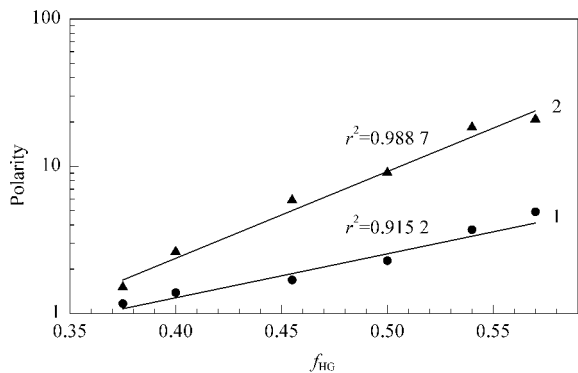

Fig. 1 P_a-f_{HG} and P_r-f_{HG} **plots of alkanolamides**
1. P_a 2. P_r.

2.2.2 K-f_{HG} relationship

K_{DIB} K_{IO} and K_{EtOH} values are given in Table 2. The relationships of K_{DIB}-f_{HG} and K_{IO}-f_{HG} of alkanolamides having $C_7 - C_{15}$ alkyl chain are plotted and represented by the following Equation 8 and Equation 9

$$K_{DIB} = 20.814\ 7 - 24.468\ 0f_{HG} \quad r^2 = 0.974\ 7 \quad 8$$
$$K_{IO} = 19.491\ 8 - 26.045\ 1f_{HG} \quad r^2 = 0.996\ 6 \quad 9$$

It is apparent from these equations that K_{DIB} and K_{IO} decrease with increasing the f_{HG} of alkanolamides. It can be seen also from data in Table 2 that K_{DIB} and K_{IO} decrease with decreasing the hydrophobic moiety of alkanolamides while with the polar ethanol solute the reverse is observed [22].

2.2.3 C_{MeOH}-f_{HG} relationship

The determination of the relative polarity of alkanolamides and polyoxyethylenated long chain amines using GC has been reported by Huebner [25] in 1962. The $C_{MeOH\ S}$ of each surfactant was determined on the column packed with this surfactant using n-C_5 to n-C_9 alkanes to produce

the calibration line the alkane scale as described [25] and exemplified in reference 4 5 11 . The $C_{MeOH\ S}$ values were converted to an empirically derived polarity index IP_S Equation 6 .

On parallel lines $C_{MeOH\ Tail}$ was determined on columns packed with non-polar n-paraffin SHT of each surfactant as described in reference 11 . From the determined $C_{MeOH\ S}$ on surfactant and $C_{MeOH\ Tail}$ on SHT $C_{MeOH\ HG}$ value of the surfactant head group HG could be derived from the following relation

$$C_{MeOH\ HG} = C_{MeOH\ S} - C_{MeOH\ Tail} \quad 10$$

Subsequently simple formula is devised to allow calculation of IP_{HG} values of certain chemical class of surfactants.

$$IP_{HG} = 100\ \log \quad C_{MeOH\ HG} - 4.7 + 60 \quad 11$$

$C_{MeOH\ S}$ on the employed surfactants and their corresponding IP_S values are plotted against the head group weight fractions of these surfactants. Plots of $C_{MeOH\ S}$-f_{HG} and IP_S-f_{HG} for alkanolamides and polyoxyethylenated long chain amines are represented by Equation 12 and Equation 13 for alkanolamides.

$$C_{MeOH\ S} = 19.264\ 3f_{HG} - 1.003\ 3 \quad r^2 = 0.986\ 3 \quad 12$$
$$IP_S = 285.463\ 0f_{HG} - 12.923\ 6 \quad r^2 = 0.998\ 6 \quad 13$$

and Equation 14 and Equation 15 for polyoxyethylenated long chain amines.

$$C_{MeOH\ S} = 16.778\ 9f_{HG} - 5.502\ 4 \quad r^2 = 0.928\ 4 \quad 14$$
$$IP_S = 444.386\ 8f_{HG} - 235.820\ 9 \quad r^2 = 0.988\ 9 \quad 15$$

It can be seen from the obtained equations that each of the determined polarity terms $C_{MeOH\ S}$ and IP_S increase with increasing f_{HG} and decreasing the hydrophobic moiety the nonpolar hydrocarbon tail of surfactant stationary phase.

The logarithmic values of $C_{MeOH\ HG}$ or IP_{HG} are plotted against f_{HG} of alkanolamides and polyoxyethylenated long chain amines. The obtained plots in Fig. 2 reveal that the polarity of alkanolamide head group $C_{MeOH\ HG}$ is higher than that of polyoxyethylenated amines. Such polarity term $C_{MeOH\ HG}$ determined by gas chromatography can be used for the distinction between the polarities of different surfactants having different hydrophilic moieties. Two simple formulas relating log IP_{HG} and f_{HG} for alkanolamides Equation 16 and polyoxyethylenated amines Equation 17 are obtained.
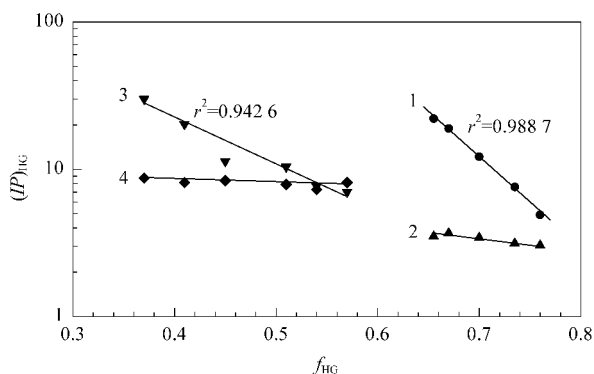
Fig. 2 IP_{HG}-f_{HG} plots of alkanolamides and polyoxyethylenated long chain amines

1. polyoxyethylenated long chain amines   2. polyoxyethylenated long chain amine head group   3. alkanolamides   4. alkanolamide head group.

$$\log \; IP_{HG} = 72.573\,6 - 119.969\,0 f_{HG} \qquad 16$$
$$\log \; IP_{HG} = 120.078\,6 - 152.821\,5 f_{HG} \qquad 17$$

2.3 *HLB* numbers of nitrogen-containing surfactants

HLB numbers of alkanolamides are calculated by applying three reported equations as shown in the experimental section. Calculated *HLB* numbers of alkanolamides are given in Table 3. *HLB* values of polyoxyethylenated long chain amines are determined through NMR analysis. *HLB* numbers from NMR analysis and that calculated by applying Equation 1 for polyoxyethylenated long chain amines are given in Table 4. It can be seen from data in Table 3 that *HLB* numbers calculated from Equation 1 are approximating that deduced from NMR analysis. This agreement between calculated and determined *HLB* numbers is rather good.

Table 3   Polarity terms $C_{MeOH\ S}$ and IP_S measured on surfactant stationary phases and their corresponding head group terms $C_{MeOH\ HG}$ and IP_{HG}

Stationary phases	R	*HLB* values				f_{HG}	$C_{MeOH\ S}$	IP_S	$C_{MeOH\ HG}$	IP_{HG}
		a	b	c	d					
Alkanolamides	C_7	–	11.42	19.95	23.5	0.571	10.21	134.12	0.81	6.91
	C_8	–	10.78	19.47	23.0	0.539	9.42	126.39	0.72	7.28
$\begin{array}{c}O\\\parallel\\R-C-N\end{array}\begin{array}{c}CH_2CH_2OH\\\\CH_2CH_2OH\end{array}$	C_9	–	10.20	19.00	22.6	0.510	8.61	119.22	0.81	10.14
	C_{11}	–	9.20	18.25	22.2	0.454	7.59	106.09	0.84	14.91
	C_{13}	–	8.38	17.10	21.9	0.409	6.73	90.75	0.83	22.83
	C_{15}	–	7.70	16.15	21.5	0.372	6.43	83.80	0.88	30.86
Polyoxyethylenated long chain amines	C_{10}	14.80	15.20	–	–	0.761	7.49	104.56	0.29	4.77
	C_{12}	14.20	14.70	–	–	0.736	6.65	89.00	0.30	7.25
$\begin{array}{c}CH_2CH_2O\ _x-H\\\\R-N\\\\CH_2CH_2O\ _y-H\end{array}$	C_{14}	13.60	14.00	–	–	0.701	6.10	74.61	0.32	11.27
	C_{16}	13.00	13.40	–	–	0.671	5.80	64.10	0.35	17.60
$x + y \cong 10$	C_{18}	12.60	13.20	–	–	0.655	5.59	55.00	0.34	20.96

a. based on NMR analysis   b. calculated by applying Equation 1 and Equation 2   c. calculated by applying Equation 3   d. calculated by applying Equation 4 .

A single straight line relation is achieved by plotting *HLB* numbers of 26 individuals of alkanolamides and polyoxyethylenated long chain amines having different hydrophobic and hydrophilic moieties against the head group weight fractions of the individuals of the two surfactant classes. Subsequently a general formula is developed.

$$HLB = 18.913\,0\,f_{HG} + 0.613\,7 \quad r^2 = 0.997\,8 \qquad 18$$

Equation 18 can be devised to allow the calculation of *HLB* values of two chemical classes alkanolamides and polyoxyethylenated long chain amines from knowledge of head group weight fraction. The investigated surfactant classes have nitrogen-containing head groups.

3 Conclusions

K_{DIB} -HLB relationship previously derived for a number of different surfactant families cannot used in the case of the investigated surfactants as K_{DIB} depend not only on its HLB numbers but also on its structural details.

Head group weight fraction f_{HG} can used as a polarity hydrophilic parameter characterizing for surfactants of different hydrophobias.

HLB-f_{HG} relationship permits calculation of *HLB* number from a knowledge of head group weight fractions of alkanolamides and polyoxyethylenated primary amines.

Table 4 *HLB* numbers and f_{HG} values of polyoxyethylenated long chain amines

R	n	Apparent molecular weight	H. G. formula weight	H. G. weight fraction f_{HG}	HLB from NMR analysis	HLB from Equation 1
$C_{10}H_{21}$	6.04	423	265.76	0.665	12.6	15.2
	5.57	490	333.08	0.711	13.7	
	9.90	593	435.60	0.761	14.8	
	11.00	641	484.00	0.779	15.2	
	14.17	781	623.48	0.819	16.1	
$C_{12}H_{25}$	5.90	445	259.60	0.583	11.7	14.7
	8.43	556	370.95	0.667	13.3	
	10.35	641	455.40	0.736	14.2	
	12.00	713	528.00	0.741	14.8	
	14.70	832	646.80	0.777	15.5	
$C_{14}H_{29}$	10.20	660	462.80	0.701	13.6	14.0
$C_{16}H_{33}$	8.40	611	369.60	0.605	12.1	13.4
	10.10	686	444.40	0.648	13.0	
	11.06	728	486.64	0.668	13.4	
	13.13	819	577.72	0.705	14.1	
	18.20	1042	800.80	0.769	15.4	
$C_{18}H_{37}$	10.60	739	466.40	0.631	12.6	13.2
	12.03	798	529.30	0.663	13.3	
	13.50	864	594.00	0.687	13.8	
	20.00	1150	880.00	0.765	15.3	

n = Average number of ethylene oxide units per amine molecule determined through NMR analysis. H. G. head group.

References

1 Rohrschneider L. In Giddings J C Keller R A eds. Advances in Chromatography Vol. 4. New York Dekker 1967. 333

2 Golovnaya R V Ansenev Yu N. Usp Khim 1973 42 2 221

3 Kováts E Weib P B. Ber Bunsenger Phys Chem 1965 69 812

4 Mostafa N E. MS Thesis . Cairo Egypt Faculty of Science Cairo University 1996

5 Barakat Y El-Kholy S A Mostafa N E El-Zein S M. Egypt J Petrol 1997 6 53

6 Rohrschneider L. J Chromatogr 1966 22 6

7 Golovnaya R V Misharina T A. Usp Khim 1980 49 171

8 McReynolds W O. J Chromatogr Sci 1970 8 685

9 Wold S Andersson K. J Chromatogr 1973 43 80

10 Rohrschneider L. Anal Chem 1973 45 1 241

11 Barakat Y Ibrahim V Mostafa N E Shaker N O. Chinese Journal of Chromatography 2005 23 4 347

12 Weil K Parris N Stirton J. J Am Oil Chemist's Soc 1970 47 91

13 Rosen M J. Characteristic Features of Surfactants. Chapter 1. New York John Wiley and Sons 1989. 19

14 McCutcheon's-Detergents & Emulsifiers. International Edition. USA MC Publishing Co 1997. 7

15 El-Kholy S A. PhD Thesis . Cairo Egypt Ain Shams University 1993

16 Fine R D . J Am Oil Chemist's Soc 1958 35 542

17 Malkemus I D Swan J D. J Am Oil Chemist's Soc 1957 34 342

18 Kiheffer J V Jungermann E Jr. Anal Chem 1960 32 1 178

19 Greff R A Flanagan P W Smith H P. J Am Oil Chemist's Soc 1963 40 118

20 Griffin W C. J Soc Cosmet Chem 1949 1 311

21 Davies J T. Proc 2nd Int Congr Surface Activity. London s. n. 1957. 426

22 Harva O Kivalo P Keltakallo A. Suomen Kemistil 1959 32B 52

23 Cvetanovic R J Duncan F J Falconer W E Irwin R S. J Amer Chem Soc 1965 87 9 1 827

24 Graciaa A Barakat Y El-Emary M Fortney L N Schechter R S Yiv S H Wade W H. J Colloid Interface Sci 1982 89 1 209

25 Huebner V R. Anal Chem 1962 34 488

26 Becher P Birkmeier R L. J Amer Chem Soc 1964 41 169

27 Petrowski G E Vanatta J R. J Amer Oil Chem Soc 1973 50 284

28 Fineman I G A. J Amer Oil Chem Soc 1969 46 296

29 Griffin W C. American Perfumer 1955 5 25

30 Haken J K. In Giddings J C Grushka E Cazes J Brown P R eds. Advances in Chromatography. New York Marcel Dekker Inc. 1979. 163

31 Mickle J B Smith W Tietz J M Titus T C Johnson M. J Food Sci 1971 36 423