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Robert Z. Greenley[a]
[a] New Enterprise Division, Monsanto Company, St. Louis, Missouri

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Determination of Q and e Values by a Least Squares Technique

ROBERT Z. GREENLEY

New Enterprise Division
Monsanto Company
St. Louis, Missouri 63166

ABSTRACT

A more precise determination of Q and e values for vinyl monomers can be attained through the use of a linear least squares technique.

INTRODUCTION

During the past year a number of authors [1-8] have sought new ways of characterizing vinyl monomers with regard to their free radical copolymerization behavior. These efforts were largely due to a dissatisfaction with the "Q and e" system postulated by Alfrey and Price [9a, 9b]. As pointed out earlier [10], the problem in using the Alfrey-Price scheme probably lies in the use of some poor experimental reactivity ratios in determining average Q and e values rather than in the actual scheme itself. The purpose of this paper is to report new Q and e values obtained by using a simple linear least squares evaluation of statistically significant reactivity ratios.

DISCUSSION

The standard Q-e equation [9a] is

$$Q_2 = Q_1/r_1 \exp[-e_1 (e_1 - e_2)] \tag{1}$$

where Q_i and e_i represent the reactivity and polarity, respectively, of a vinyl monomer, and $r_1 = k_{11}/k_{12}$, the ratio of the reactivity of a monomer radical with that monomer to the reactivity of the same radical with a comonomer. After converting from the exponential form to a logarithmic form, Eq. (1) can be rearranged to

$$[(\ln Q_1/r_1) - e_1^2] = -e_2 e_1 + \ln Q_2 \tag{2}$$

This latter equation can be solved for $-e_2$ (slope) and $\ln Q_2$ (intercept), representing the unknown monomer, by plotting $[\ln Q_1/r_1) - e_1^2]$ vs e_1. The Q_1 and e_1 values are from other previously characterized monomers whose reactivity ratio (r_1) with the unknown monomer had been determined. A linear least squares evaluation [11] of the data facilitated the evaluation of Q_2 and e_2.

The first requirement for the utilization of Eq. (2) was the selection of a small group of common monomers for which Q and e values could be independently established. Since by definition the Q-e scheme is based on styrene ($Q = 1.0$, $e = -0.8$) [9b], the average Q and e values of the monomers in this primary group were calculated from Eqs. (1) and (3) [9a]:

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{1/2} \tag{3}$$

utilizing only their reactivity ratios with styrene. The six primary monomers, acrylic acid, acrylonitrile, butadiene, methyl acrylate and methyl methacrylate, were chosen because their reactivity ratios with styrene had been narrowly defined by several investigators. The reactivity ratios used in these and all subsequent calculations were taken from the compilation by Young [12].

The Q and e values of a secondary group of 10 common vinyl monomers were determined using Eq. (2) with the primary monomer group supplying the Q_1 and e_1 values. The Q and e values for a tertiary set of monomers which had four or more reactivity ratio citations in Young's listing were then determined using the Q and e values of the primary and secondary groups in the least squares calculation.

The Q and e values developed for the three groups during this first

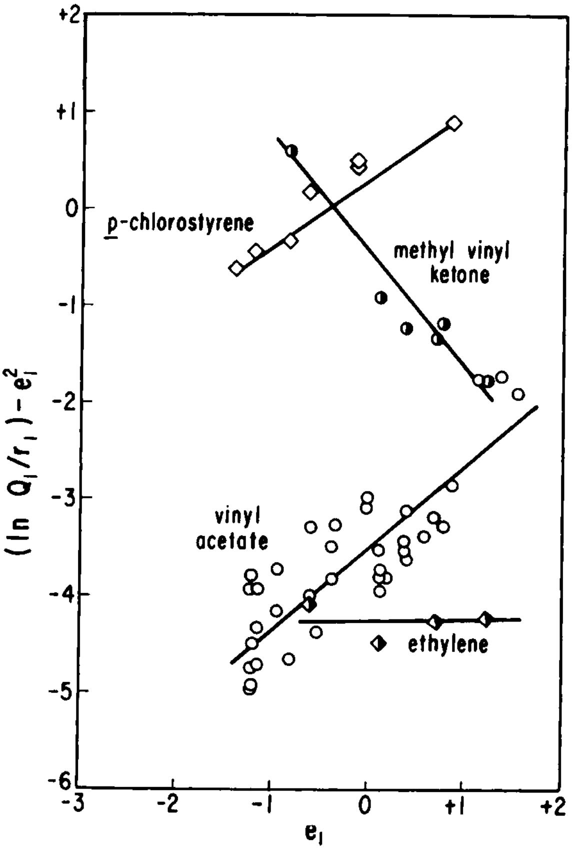

FIG. 1. Graphical representation of the solution of $(\ln Q_1/r_1) - e_1^2 = -e_2e_1 + \ln Q_2$ for four monomers where $-e_2$ is the slope and $\ln Q_2$ is the intercept.

pass through the data were subsequently used to recalculate the Q and e values for the secondary and tertiary groups. Group I was not redetermined so that the styrene bias of the system could be better maintained. After four iterations, no significant changes in the Q and e values for Groups II and III were observed. During the iterative development of these two groups, a number of reactivity ratio citations were dropped due to their lack of fit with the majority of the data points. A typical graphical representation of the process is shown in Fig. 1.

The final Q and e values for the three groups were then used to determine the Q and e values of other monomers with four or more reactivity ratio citations and monomers with three citations. Monomers with less than three citations were not evaluated.

RESULTS

The new Q and e values are listed in Table 1 according to group. Also included in the table are the number of reactivity ratio citations used (No.) for a given monomer evaluation and the correlation coefficient (r) [11] for the calculation. The Q and e values in the table are considered as good a characterization of monomer copolymerization behavior as the available data will permit. The results in Group V, however, must be used with caution due to the low correlation coefficients for many of the monomers.

Several interesting observations can be made concerning this new Q-e map. The polarity of ethylene is very close to zero, $e = -0.02$ [7]. The polarities of similar monomers such as alkyl vinyl ethers, acrylate esters, and methacrylate esters are more closely grouped as shown in Table 2.

Acrylamide and acrolein were not included in Table 1 due to the disparate nature of their reactivity ratios.

CONCLUSIONS

With the development of better techniques for determining reactivity ratios [13, 14] and this least squares method for calculating Q and e values, free radical copolymerization of vinyl monomers can become a more exact science.

TABLE 1. Q and e Values of Vinyl Monomers

Monomer	Q	e	No.[a]	r[b]
I				
Acrylic acid	1.25 ± 0.26	+0.88 ± 0.16		
Acrylonitrile	0.48 ± 0.08	+1.24 ± 0.08		
Butadiene	3.62 ± 2.3	-1.36 ± 0.23		
Methacrylonitrile	0.85 ± 0.14	+0.79 ± 0.13		
Methyl acrylate	0.44 ± 0.00	+0.60 ± 0.09		
Methyl methacrylate	0.75 ± 0.04	+0.38 ± 0.07		
Styrene	1.0	-0.80		
II				
Butyl acrylate	0.30	+0.74	(14)	0.83
2-Chlorobutadiene	5.6	+0.51	(9)	.82
2,5-Dichlorostyrene	1.36	+0.68	(10)	.85
Isoprene	1.34	-0.44	(10)	.86
Methyl vinyl ketone	0.62	+1.11	(6)	.94
Vinyl acetate	0.031	-0.84	(36)	.84
Vinyl chloride	0.056	+0.20	(30)	.43
Vinylidene chloride	0.26	+0.40	(25)	.59
2-Vinylpyridine	1.32	-0.38	(11)	.94
N-Vinylpyrrolidinone	0.12	-1.09	(8)	.92
III				
Allyl acetate	0.033	-0.61	(7)	0.79
Allyl chloride	0.033	+0.04	(12)	.10

(continued)

TABLE 1 (continued)

Monomer	Q	e	No.[a]	r[b]
Bicyclo[2.2.1]-2,5-heptadiene	0.075	-0.63	(5)	.61
Butyl methacrylate	0.66	+0.34	(7)	.68
Butyl vinyl sulfonate	0.10	+1.26	(5)	.84
2-Chloroallyl acetate	0.22	-0.98	(5)	.65
p-Chlorostyrene	1.32	-0.65	(8)	.97
Chlorotrifluoroethylene	0.019	+1.06	(5)	.82
Crotonic acid	0.015	+1.11	(5)	.95
Diethyl fumarate	0.30	+2.17	(7)	.83
Diethyl maleate	0.044	+0.81	(10)	.80
Dimethyl itaconate	0.75	+0.70	(6)	.90
N,N-Divinylaniline	0.14	-0.70	(5)	.72
Ethyl acrylate	0.41	+0.46	(6)	.93
Ethylene	0.012	-0.02	(4)	.60
Ethyl methacrylate	0.57	+0.35	(4)	.66
Ethyl vinyl ether	0.025	-1.72	(6)	.98
5-Ethyl-2-vinylpyridine	1.26	-0.95	(4)	.96
2-Fluorobutadiene	2.27	+0.69	(5)	.74
Glycidyl methacrylate	1.03	+0.32	(4)	.92
Isobutylene	0.029	-1.06	(6)	.84
Isobutyl methacrylate	0.62	+0.09	(4)	.57
Isopropenyl isocyanate	0.18	-1.05	(8)	.93
Maleic anhydride	0.51	+3.17	(15)	.79
Methacrylic acid	1.38	+0.59	(6)	.87
Methallyl chloride	0.095	-0.66	(4)	.50
Methyl isopropenyl ketone	0.96	+0.65	(4)	.80

p-Methoxystyrene	1.45	-1.20	(5)	.95
α-Methylstyrene	0.84	-0.64	(8)	.92
p-Methylstyrene	1.09	-0.59	(4)	.98
2-Methyl-5-vinylpyridine	0.85	-0.35	(7)	.74
Tetrachloroethylene	0.001	+1.42	(9)	.98
Trichloroethylene	0.011	+1.30	(10)	.95
cis-Trimethyl aconitate	0.20	+1.52	(4)	.94
Vinyl benzoate	0.029	-0.59	(6)	.88
N-Vinylcarbazole	0.28	-1.02	(9)	.88
Vinylene carbonate	0.008	-0.71	(5)	.96
Vinyl formate	0.13	-0.37	(5)	.46
Vinylidene cyanide	33.	+0.87	(9)	.22
Vinyl isocyanate	0.13	-0.90	(7)	.94
Vinyl-12-ketostearate	0.031	-0.44	(4)	.59
Vinyl nonanoate	0.029	-0.36	(5)	.57
Vinyl octadecanoate	0.037	-0.94	(6)	.84
N-Vinyloxazolidone	0.064	-1.21	(8)	.92
Vinyl pinonate	0.026	-0.55	(5)	.67
4-Vinylpyridine	1.03	-0.08	(5)	.36
N-Vinylsuccinimide	0.12	-0.61	(5)	.88
Vinyl undecenoate	0.041	-0.69	(6)	.88
		IV		
p-Bromostyrene	1.52	-0.46	(4)	0.44
2-Chloroallyl alcohol	0.11	-1.16	(5)	.96
2-Chloroethyl acrylate	0.61	+0.69	(4)	.75
Ethyl vinyl oxalate	0.066	-0.03	(4)	.10
Hydronopyl acrylate	0.31	+0.71	(4)	.88
Methacrolein	0.33	-1.04	(4)	.67

(continued)

TABLE 1 (continued)

Monomer	Q	e	No.[a]	r[b]
Methacrylamide	0.61	+0.98	(6)	.24
Methacryloxymethyl pentamethyldisiloxane	0.40	-0.45	(4)	.47
N-Methylolacrylamide	0.33	+0.66	(4)	.98
Methyl vinyl sulfone	0.069	+0.94	(4)	.61
Octyl vinyl ether	0.028	-1.66	(5)	.91
Sodium acrylate	0.50	+2.54	(4)	.92
tris-(Trimethyl siloxy) vinylsilane	0.036	-1.28	(5)	.98
Vinyl cinnamate	0.25	+1.41	(4)	.81
		<u>V</u>	(3)	
1-Acrylamide-1-deoxy-D-glucitol	0.15	-0.17		0.27
N-Allylstearamide	0.046	+0.37		.96
Butyl vinyl ether	0.13	-1.99		.58
o-Chlorostyrene	1.17	-0.28		.99
1-Deoxy-1-methacrylamide-D-glucitol	0.16	-0.02		.02
Diallylmelamine	0.016	-0.92		.85
Dibutyl Itaconate	0.67	+0.27		.60
1,1-Dihydroperfluorobutyl acrylate	0.67	+0.77		.95
N,N-Dimethylacrylamide	0.55	-0.56		.65
1,1-Diphenylethylene	1.15	-0.97		.74

Ethyl-α-acetoxyacrylate	0.50	+0.77	.99
N-Ethyl-N'-vinylurea	0.16	-2.07	.99
Fumaronitrile	0.62	+2.39	.70
Hexafluorobutadiene	0.82	+0.39	.71
Isopropenyl acetate	0.021	-0.34	.93
Maleimide	0.74	+2.45	.99
Methacrylic anhydride	1.50	+1.75	.81
Methallyl acetate	0.036	-1.97	.99
Methyl-α-chloroacrylate	1.68	+0.51	.80
N-Methylcitraconimide	0.77	+1.47	.91
Methyl vinyl sulfide	0.20	-2.36	.82
N-Methyl-N-vinyl-p-toluene sulfonamide	0.089	-0.86	.99
2-Nitrobutyl acrylate	0.46	+0.99	.98
m-Nitrostyrene	1.98	-0.03	.03
N-n-Octadecylacrylamide	0.37	+0.81	.84
n-Octadecyl vinyl ether	0.015	-1.72	.99
Octyl acrylate	0.62	+1.99	.99
Pentachlorostyrene	0.19	+0.91	.94
Phenylacetylene	0.34	-0.23	.67
Phenyl vinyl ether	0.17	+1.00	.92
Triallyl cyanurate	0.013	-0.12	.13
Triallyl isocyanurate	0.012	-0.26	.33
3,3,3-Trichloropropene	0.032	+1.08	.99
Vinyl bromide	0.030	+0.07	.18
Vinyl butanoate	0.029	-1.02	.94
Vinyl chloroacetate	0.051	-1.43	.98
Vinyl laurate	0.012	-0.41	.66

(continued)

TABLE 1 (continued)

Monomer	Q	e	No.[a]	r[b]
Vinylmesitylene	0.19	-0.17		.15
Vinyl propionate	0.042	-0.63		.70
2-Vinylquinoline	1.28	-0.66		.72
Vinyl trimethoxysilane	0.032	+0.16		.27

[a] No. = number of reactivity ratio citations used in the calculation.

[b] r = correlation coefficient.

TABLE 2. Comparative Polarities of Similar Monomers

	e Value	
	New	Old [12]
A. Alkyl Vinyl Ethers		
Ethyl	-1.72	-1.17
Octadecyl	-1.72	-0.63
Octyl	-1.66	-0.79
Average	-1.70 ± 0.03	-0.86 ± 0.20
B. Alkyl Acrylate Esters		
Butyl	+0.74	+1.06
Chloroethyl	+0.69	+0.54
Ethyl	+0.46	+0.22
Methyl	+0.60	+0.60
Average	+0.62 ± 0.09	+0.60 ± 0.22
C. Alkyl Methacrylate Esters		
Butyl	+0.34	-0.23
Isobutyl	+0.09	-0.04
Ethyl	+0.35	+0.17
Methyl	+0.38	+0.40
Average	+0.29 ± 0.10	+0.08 ± 0.21

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