Deprotonation of 5-Nitroindole and its 2-Carboxylate Ion in Twin-tailed Surfactants

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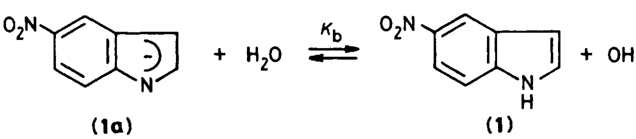
Deprotonations of 5-nitroindole (**1**) and its 2-carboxylate ion (**2**) at high pH are increased by self-assemblies of didodecyldimethylammonium chloride and hydroxide (DDDACl and DDDAOH). The increased deprotonation can be accounted for quantitatively in terms of binding of OH^- and the indicators to the colloidal self-assemblies. Basicity constants in the self-assemblies are similar to those in micelles of cetyltrimethylammonium chloride, bromide, and hydroxide (CTACl, CTABr, and CTAOH) and are slightly smaller than in water.

Reaction rates and equilibria in water are markedly affected by a variety of colloidal species.[1] Some, for example micelles and oil-in-water microemulsions,[2] are self-assembling, but others, for example, synthetic vesicles, are metastable and their formation depends on the input of energy by sonication or evaporation.[1,3,4]

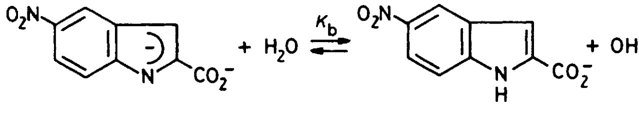
Evans, Ninham, and their co-workers have pointed out that formation of colloids from monomeric surfactants is influenced by the packing of monomers into the colloidal particle.[5] They have shown that didodecyldimethylammonium salts (DDDAX) are reasonably soluble in water, provided that counterions are hydrophilic, *e.g.* OH^-, F^-, or formate.[6] They postulate that vesicles form spontaneously in dilute solution, but with increasing [surfactant] (> 0.1M), solutions become very viscous, and extended micelle-like structures form. If the counterion is less hydrophilic, *e.g.*, Br^-, the salts are only sparingly soluble in water. There is physical evidence for vesicle formation only if the counterion is very hydrophilic and binds weakly to the colloidal assembly, which will therefore have a high apparent charge.

Dioctadecyldimethylammonium chloride is not soluble in water, but vesicles can be generated by sonication or evaporation, and they markedly speed bimolecular reactions of nucleophilic anions.[3,4] Nucleophilic substitution by OH^- is speeded by spontaneously forming assemblies of didodecyldimethylammonium chloride and hydroxide.[7,8] The rate enhancements have a similar origin to those in normal micelles, and can be related to concentration of reagents in the small colloidal particles.

The first examples of micellar effects on chemical reactions were on acid–base equilibria, and deprotonation of weak acids in dilute solutions of OH^- and cationic micelles has been treated quantitatively by estimating the distribution of OH^- and the indicator between water and micelles.[9–12]



(**1a**) (**1**)



(**2a**) (**2**)

We have examined deprotonations of 5-nitroindole (**1**) and its 2-carboxylate ion (**2**) in solutions of DDDAOH and DDDACl + NaOH, and compared the surfactant effects with those of cetyltrimethylammonium chloride, bromide, and hydroxide.[11] The effects upon the indicator deprotonation should be related to the availability of OH^- at the surface of the colloidal particle[13] and similarities, or otherwise, between the surfaces of colloidal particles of DDDAX or CTAX [$C_{16}H_{33}NMe_3X$ (X = OH, Cl, or Br)]. Deprotonation of (**1**) and (**2**) has been examined in micelles of CTAOH and CTABr.[11] Yagil[14] calculated K_B 5.6 and 8.3 mol^{-1} l for (**1**) and (**2**) in water.

Results and Discussion

Deprotonation in CTACl *and* DDDACl.—Extents of deprotonation, *f*, go through maxima with increasing [surfactant] (Figures 1—4). These maxima are in very dilute surfactant and with CTACl (and CTABr) are below the critical micelle concentration (c.m.c.) which is 1.3 × 10^{-3}M in water.[15] Other indicators, *e.g.*, phenols and arylimidazoles, behave similarly in CTACl or CTABr,[10a,16] and anionic forms of the indicators probably bind to the monomeric surfactant cations, or to submicellar aggregates of them.[13] We see sharp increases in *f* in very dilute DDDACl and the maxima are at lower

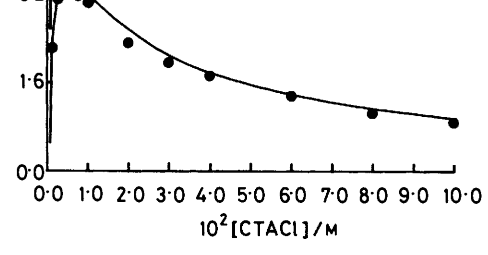


Figure 1. Extent of deprotonation of 5-nitroindole in CTACl + NaOH: (●) 0.01M- and (■) 0.1M-NaOH

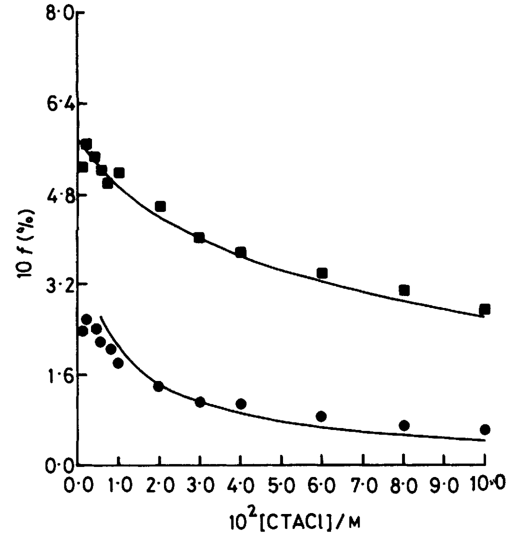


Figure 2. Extent of deprotonation of 5-nitroindole-2-carboxylate ion in CTACl + NaOH: (●) 0.01M- and (■) 0.1M-NaOH

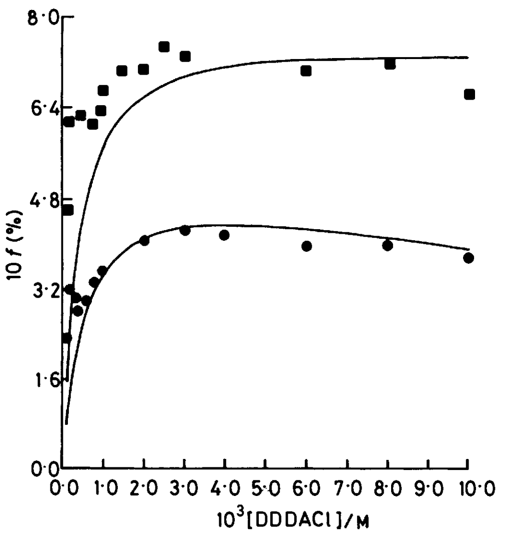


Figure 3. Extent of deprotonation of 5-nitroindole in DDDACl + NaOH: (●) 0.01M- and (■) 0.1M-NaOH

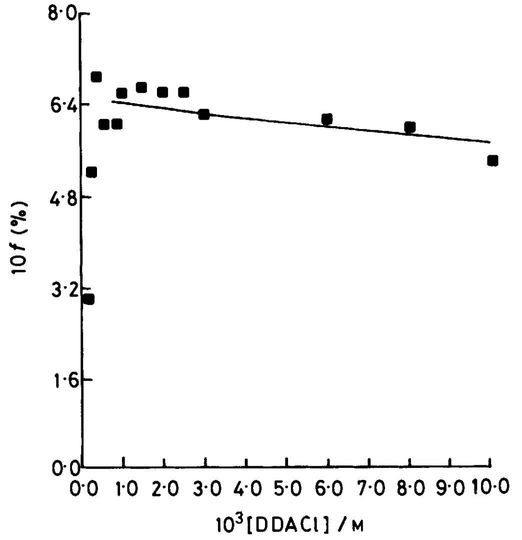


Figure 4. Extent of deprotonation of 5-nitroindole-2-carboxylate ion in DDDACl + NaOH (0.1M)

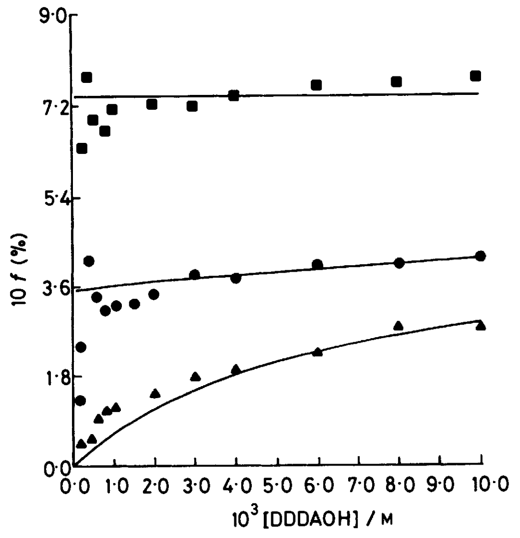


Figure 5. Extent of deprotonation of 5-nitroindole in DDDAOH: (▲) no added NaOH, (●) 0.01M-NaOH, (■) 0.1M-NaOH

concentrations than found with CTACl or CTABr, suggesting that the twin-chain surfactants assemble in very dilute solution and we neglect the concentration of monomeric surfactant.

Deprotonation in DDDAOH.—Extents of deprotonation increase with increasing DDDAOH and are further increased by added [OH$^-$]. This behaviour is very similar to that found with CTAOH[11] (Figures 5 and 6).

Quantitative Treatment of Deprotonation.—The variations of f were fitted to equations which consider distribution of indicator and OH$^-$ between water and colloidal assemblies in terms of β, the fractional neutralization of head groups by counterions, and an exchange parameter, $K_{\rm Cl}^{\rm OH}$, or a binding parameter, $K'_{\rm OH}$. Values of these parameters were similar to those used in fitting kinetic data,[8] and we assumed that the association constant, K_s, of 5-nitroindole would be similar to that in CTAOH or CTABr,[11a] and that the anion would bind quantitatively.[11b] We also assumed that 5-nitroindole-2-carboxylate ion and the related dianion would bind quantitatively. This assumption is reasonable, although it probably fails with high concentration of added halide ion, because of competition between it and the indicator anions.[12] We did not examine very low [surfactant] because we had to use *ca.* 9 × 10^{-5}M-indicator.[11]

We write the base dissociation constant, $K_{\rm B}^{\rm M}$, in the colloidal assemblies as equation (1)[10a,11] where BH is the protonated

$$K_{\rm B}^{\rm M} = [{\rm BH_M}]m_{\rm OH}^{\rm s}/[{\rm B_M^-}] \qquad (1)$$

form of the indicator, and $m_{\rm OH}^{\rm s}$ is the mol ratio of bound OH$^-$ ([OH$_{\rm M}^-$]), to cationic head groups in the colloids assembly {equation (2) where [D$_n$] is associated surfactant (detergent)}.

$$m_{\rm OH}^{\rm s} = [{\rm OH_M^-}]/[{\rm D}_n] \qquad (2)$$

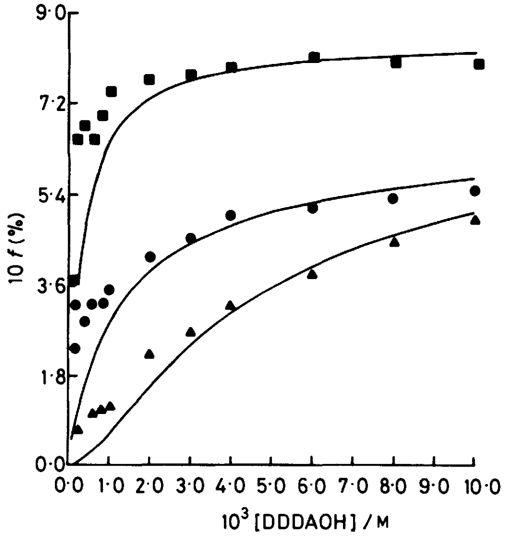


Figure 6. Extent of deprotonation of 5-nitroindole-2-carboxylate ion in DDDAOH: (▲) no added NaOH, (●) 0.01M-NaOH, (■) 0.1M-NaOH

The fraction of deprotonation, f, and K_B^M are related by equations (3) and (4) where $K_B(\text{app})$ is the overall base dissociation constant.

$$K_B(\text{app}) = K_B^M[OH_T^-]/m_{OH}^s \qquad (3)$$

$$f = [OH_T^-]/\{[OH_T^-] + K_B(\text{app})\} \qquad (4)$$

The binding of 5-nitroindole (BH) is assumed to follow equation (5).[17] Competition between Cl^- and OH^- is written in terms of equation (6).[8,13,18]

$$[BH_M]/[BH_T] = K_s[D_n]/(1 + K_s[D_n]) \qquad (5)$$

$$K_{Cl}^{OH} = [OH_W^-][Cl_M^-]/[OH_M^-][Cl_W^-] \qquad (6)$$

The colloidal surface is assumed to be saturated with counterions, *i.e.*, β, the degree of counterion binding is constant.[13] The mol ratio, m_{OH}^s, can then be calculated as a function of $[OH^-]$ and $[D_n]$ following the procedures already described.[8,11]

Binding of OH^- in DDDAOH is assumed to follow the mass-action-like equation (7).[8,19,20]

$$K'_{OH} = [OH_M^-]/\{[OH_W^-]([D_n] - [OH_M^-])\} \qquad (7)$$

Estimation of K_B^M.—A simple computer program allowed us to predict variations of f with [CTACl] or [DDDAX] for assumed values of K_B^M.[11] For CTACl we used values of K_{Cl}^{OH} 4—5 and β 0.7 which are in the range used in fitting a variety of kinetic data and are similar to values measured by physical methods.[13,21] Values of K_s for 5-nitroindole were expected to be similar to those estimated for binding to micelles of CTABr.[11a] We used similar values for DDDACl, based on kinetic data.[8]

For DDDAOH we took K'_{OH} 55 l mol^{-1} because this value is that estimated for CTAOH[19] and is consistent with kinetic data.[8]

Table 1. Deprotonation of 5-nitroindole[a]

Surfactant	[NaOH]/M	K_S/l mol^{-1}	K_B^M	K_B/K_B^V
CTACl	0.01	300	0.27	3.0
CTACl	0.1	400	0.21	3.8
DDDACl	0.01	300	0.23	3.5
DDDACl	0.1	450	0.16	5.0
CTABr	0.01	350	0.14	5.7[b]
CTABr	0.1	400	0.15	5.3[b]
DDDAOH		400	0.22	3.6
DDDAOH	0.01	400	0.27	3.0
DDDAOH	0.1	450	0.15	5.3
CTAOH		300	0.14	5.7[b]
CTAOH	0.1	400	0.09	8.9[b]

[a] Calculated taking β 0.7 for CTACl and DDDACl, K_{Cl}^{OH} 5 and 4 for CTACl and DDDACl respectively, K'_{OH} 55 l mol^{-1} and 10^4 c.m.c. 7 and 5M for CTACl in 0.01 and 0.1M-NaOH. [b] Ref. 11*a*.

Table 2. Deprotonation of 5-nitroindole-2-carboxylate ion

Surfactant	[NaOH]/M	K_B^M	K_B/K_B^V
CTACl	0.01	0.65	1.8
CTACl	0.1	0.55	2.2
DDDACl	0.1	0.37	3.2
CTABr	0.01	0.75	1.6[b]
CTABr	0.1	0.60	2.0[b]
DDDAOH		0.70	1.7
DDDAOH	0.01	0.65	1.8
DDDAOH	0.1	0.30	4.0
CTAOH		0.75	1.6[b]
CTAOH	0.1	0.60	2.0[b]

[a] Calculated taking β 0.7 and K_{Cl}^{OH} 5 for CTACl and DDDACl, K'_{OH} 55 l mol^{-1} and 10^4 c.m.c. 7 and 5M for CTACl in 0.01 and 0.1M-NaOH. [b] Ref. 11*b*.

The fits to experiment are shown in Figures 1—6 in which all the lines are calculated and the parameters are in Tables 1 and 2. Agreement is worst for experiments in DDDAOH and DDDACl, because here we were restricted in the range of [surfactant]. Solutions of DDDAOH become very viscous and the colloidal particles change structure as concentration is increased[5b,6] and DDDACl has limited solubility in water. The treatment is unsatisfactory for very dilute surfactants because of interaction between the indicators and monomeric surfactant or small aggregates of it.

The fits for data in CTACl and DDDACl depend upon the combination of values of the various parameters [equations (2), (5), and (6)] and equally satisfactory fits can often be obtained with a variety of combinations.[21a] However, the values which we use are supported by independent measurements.[13,21] The binding constants, K_s, tend to increase with increasing $[OH^-]$ as seen in other systems due to the electrolyte 'salting out' the substrate from water and into the micelles.[10a,19]

For deprotonation of 5-nitroindole carboxylate ion (**2**) in DDDAOH the only adjustable parameters are K'_{OH} and K_B^M, because we assume complete binding of both mono- and dianionic indicator,[11b] and the variation of f with [DDDAOH] depends essentially on K'_{OH_M}.

Variations of K_B^M are not large (Tables 1 and 2), but K_B^M tends to decrease at high $[OH^-]$.

Basicity Constants in Water and Colloidal Assemblies.—Values of K_B^M are similar in micelles of CTACl, CTABr, and CTAOH and self-assemblies of DDDAOH and DDDACl (Tables 1 and 2) and some of the differences may be due to experimental limitations. Also the indicators are probably binding to small assemblies, at least with dilute surfactant, and equations (1), (2), and (5)—(7) are based on the assumption that we are dealing with monodisperse systems. Dilute solutions of CTACl and CTABr do not seem to be highly disperse,[22] and this is probably also true for solutions of CTAOH + NaOH,[23] except in very dilute solution.[19] Evans and his co-workers have concluded that self-assemblies in dilute DDDAOH are also reasonably monodisperse.[5,6] However, the largest deviations of K_B^M from the mean values were found with DDDAOH and 0.1M-NaOH, which would agree with a change in particle size or shape in these conditions.[5]

Classical values of K_B in water are generally written in terms of molar concentrations, whereas K_B^M is dimensionless [equation (2)]. Comparison of the constant in water and self-assemblies requires conversion of m_{OH}^s into a molarity, based on equation (8). Estimate of the molar volume of reaction, V_M, range from

$$K_B^V = K_B^M/0.14 \qquad (8)$$

0.14 to *ca.* 0.35 dm^3,[13,21a,d,24] and we used the lower value, although it may vary from one system to another.

Values of K_B^V mol l^{-1} are compared directly with K_B in water in Tables 1 and 2. Consistently, K_B^V is slightly smaller than K_B in water, and for arylimidazoles K_B/K_B^V *ca.* 2 (differences would be larger had we taken higher values of V_M). These comparisons depend on the assumed value of V_M, but variations are probably within a factor of 2,[13] so our conclusions about basicity are qualitatively reasonable. In addition values in the fitting parameters (Tables 1 and 2) may actually be related to differences in V_M.

These comparisons suggest that the deprotonations are taking place in a water-like environment[25] for micelles of CTA and assemblies of DDDA. Effects due to medium effects are relatively unimportant, although the cationic colloids seem to stabilize the conjugate bases relative to the other species. This effect is general and is probably due to favourable interactions between cationic head groups and charge-delocalized anions.[10–12]

Moss and his co-workers have carefully explored the possibility of exo- and endo-vesicular reactions in synthetic systems.[26] Vesicle walls are readily penetrated by nonionic solutes, but less readily by some ions.

Evans and his co-workers discuss the possibility that assemblies of DDDAOH have 'outside' and 'inside' surfaces.[5] Analysis of rates of reaction of OH$^-$ with dinitrochloroarenes[7,8] show that if such surfaces exist either both OH$^-$ and substrate move readily between them, or neither move, which is most improbable. In our deprotonation experiments 5-nitroindole and its conjugate base and the 2-carboxylate mono- and dianion should differ in their ability to penetrate vesicle walls, but we see no obvious differences between the effects of micelles and DDDA assemblies in deprotonation of indicators of different charge. Our conclusion is that, regardless of possible differences in internal structure, CTA and DDDA surfactants have similar effects on reaction rates and equilibria, although there are small differences in the fitting parameters (Tables 1 and 2).

Discussions of micellar effects upon ionic reactions are typically based on a pseudophase model in which micelles and water are treated as distinct, but uniform reaction media,[13,27] and we have followed this approach in our discussion (we neglect deprotonation in the water in view of the weak acidity of the indicators[14]).

This model rationalizes a great deal of disparate evidence, but it has serious limitations. For example in its simplest form it fails to predict variations of rate constant with [surfactant] for other than low concentrations of OH$^-$ (or H$_3$O$^+$).[28] In addition equation (7), although it implies site binding of OH$^-$ to the surface of a cationic colloid, is probably approximating the radial distribution of OH$^-$ away from that surface,[29,30] and is therefore valid only over a limited range of [OH$^-$].

Another question is that of the location of the indicators and their conjugate bases at the micellar surface. Non-ionic solutes bind because of hydrophobic and dispersive interactions, whereas coulombic interactions probably dominate the binding of hydrophilic counterions. But if the counterion is not very hydrophilic both non-specific, coulombic, and specific, short-range dispersive and hydrophobic interactions should be important.[29] The pseudophase model is based on the premise that micellar reactions occur in a uniform region at the micellar surface which is generally identified with the Stern layer, which encompasses the micellar head groups.[13,27] Polar molecules and ions of low hydrophilicity are almost certainly located in this region, but very hydrophilic ions are probably distributed according to the Poisson–Boltzmann equation as applied to coulombic interactions.[29]

This conclusion is supported by the demonstration that ion-exchange parameters for hydrophilic anions [equation (6)] estimated from fluorescence quenching by Br$^-$ do not agree with those measured kinetically or by other physical methods.[30] The agreement is reasonable for ions that are less hydrophilic than OH$^-$ of F$^-$.

Coulombic interactions are much stronger for di- than for mono-ions,[29,31] so that SO$_4^{2-}$, for example, is strongly micellar-bound,[32] but only by coulombic attraction, although Br$^-$, which is less weakly bound, interacts both specifically and coulombically.[33] The conclusions that β is independent of electrolyte is therefore suspect, although it may be reasonably correct when concentration of halide ion is much greater than [OH$^-$], because of the stronger binding by halide ion.[13,21]

These considerations also apply to the binding of the indicators used in our work, because coulombic interactions between the micelle and the dianion (**2a**) should be very strong whereas specific, short-range interactions will be more important in the binding of the other indicator species [equation (5)]. Identification of the region of reaction with the micellar Stern layer is an oversimplification for reactions involving hydrophilic ions, although the simple pseudophase, ion-exchange treatment is remarkably successful in treating micellar effects upon a variety of bimolecular ionic reactions.[13,27]

Nome and his co-workers find that the ion-exchange treatment does not fit rates of elimination at high [OH$^-$] and postulate an additional reaction path between micellar-bound substrate and OH$_W^-$.[28] We do not think it necessary to invoke this additional reaction path and in any case it would not apply to our deprotonation equilibria. Instead we believe that a complete description of micellar effects on rates and equilibria involving OH$^-$ requires abandonment of the artificial distinction between reactions in the micellar and aqueous pseudophases. However, the ability of equations (1), (2), and (5)—(7) to fit micellar effects upon reaction rates and equilibria shows that, despite its lack of theoretical underpinning, the pseudophase model is very useful on a purely empirical basis, over a limited range of concentration of hydrophilic ions for reactions in micelles and in assemblies of the didodecylammonium ions.

Experimental

Materials.—Preparation and purification of surfactants and indicators has been described.[7,8,11] Solutions were made up in distilled water under N$_2$ to exclude CO$_2$.

Deprotonation.—The fraction f of deprotonated indicator was measured spectrophotometrically at 25 °C. The indicator concentrations were 9×10^{-5}M and $f = \{[(\mathbf{1a})]/[(\mathbf{1})] + [(\mathbf{1a})]\}$ or $\{[(\mathbf{2a})]/[(\mathbf{2})] + [(\mathbf{2a})]\}$. The measurements were made at 398 and 393 nm for (**1**) and (**2**), respectively.[11]

When concentrations of DDDACl or DDDAOH were very low (2×10^{-4}M) some f values were apparently higher than expected, but we did not see this behaviour at higher [surfactant]. These anomalous results might have been due to formation of sparingly soluble ion pairs of the surfactant cation and indicator anion, and these salts, if formed, would dissolve in more concentrated surfactant.

The method of preparation of DDDA solutions, or their sonication, did not affect the results, *cf.* refs. 7 and 8. The physical properties of very dilute DDDAOH are discussed in refs. 5 and 8.

Acknowledgements

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