The Ionic Products of Water and Methanol in Methanol–Water Mixtures

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The ionic products and acid ionization constants of water and methanol in methanol–water mixtures at 25 °C have been calculated from the apparent ionic products of the solvent mixtures and the free energies of transfer of the proton from water to methanol–water mixtures. Methanol is a stronger acid than water over the entire range of solvent composition, the difference in acid strength becoming greater as the methanol content of the solvent is increased.

KOSKIKALLIO [1] measured the apparent ionic product of methanol–water mixtures but did not deduce the separate contributions to the ionic product of the ionization of water and of methanol. Gaboriaud *et al.*[2] calculated the ratios of hydroxide ions to methoxide ions in the solvent mixtures and obtained reasonable agreement between calculated ionic products and the experimental values. The present paper describes a new approach to the calculation of the separate ionic products of water and methanol in methanol–water mixtures.

TABLE 1

The apparent ionic product of methanol–water mixtures at 25 °C; units of K_S are mol^2 kg^{-2}

MeOH/ % (w/w)	X_{MeOH}	pK_S	MeOH/ % (w/w)	X_{MeOH}	pK_S
0	0	13·997 [a]	60	0·4575	14·127 [c]
10	0·0588	14·037 [c]	70	0·5675	14·218 [c]
20	0·1232	14·055 [b]	80	0·6922	14·423 [c]
28·5	0·1831	14·067 [c]	90	0·8350	14·845 [b]
50	0·3599	14·097 [c]	100	1·0000	16·708 [b]

[a] Ref. 4. [b] Ref. 1. [c] Values interpolated from data in ref. 1.

The apparent ionic product K_S (Table 1) for a methanol–water mixture is given by equation (1) [1] in

$$K_S = m_{H^+}(m_{OH^-} + m_{OMe^-}) = K_w + K_m \qquad (1)$$

which m_{H^+} represents the sum of the molalities of H_3O^+ and $MeOH_2^+$ and K_w and K_m are the ionic products of water and methanol respectively in the solvent mixture. The separate contributions of K_w and K_m to K_S were evaluated as follows.

K_{H_2O} and K_{MeOH} are equilibrium constants, defined by equations (2) and (3), for the ionization [equations (4) and (5)] of water and methanol respectively in a

$$K_{H_2O} = (a_{H^+}a_{OH^-}/a^w_{H_2O}) \qquad (2)$$

$$K_{MeOH} = (a_{H^+}a_{OMe^-}/a^m_{MeOH}) \qquad (3)$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (4)$$

$$MeOH \rightleftharpoons H^+ + OMe^- \qquad (5)$$

methanol–water mixture. In equations (2) and (3) the activities a_{H^+}, a_{OH^-}, and a_{OMe^-} refer to the solvent mixture as standard state and therefore for the pure solvent $a_{H^+} = m_{H^+}$, $a_{OH^-} = m_{OH^-}$, and $a_{OMe^-} = m_{OMe^-}$. Hence combination of equations (1)—(3) leads to equation (6)

$$K_S = K_{H_2O}a^w_{H_2O} + K_{MeOH}a^m_{MeOH} \qquad (6)$$

in which $a^w_{H_2O}$ is the molal activity of water referred to pure water standard state and a^m_{MeOH} is the molal activity of methanol referred to pure methanol standard state. The acid ionization constant $K^w_{H_2O}$ of water in water is related to a_{H^+} and a_{OH^-} for a methanol–water mixture by equation (7) in which γ_{H^+} and γ_{OH^-} are activity coefficients defined by equation (8) where μ°_w is the chemical potential of an ion in a hypothetical 1*m* ideal solution in water and μ°_s is the chemical potential of the same ion in a hypothetical 1*m* ideal solution in the solvent S.[3] Similarly the acid ionization constant

$$K^w_{H_2O} = (a_{H^+}\gamma_{H^+}a_{OH^-}\gamma_{OH^-}/a^w_{H_2O}) = K_{H_2O}\gamma_{H^+}\gamma_{OH^-} \qquad (7)$$

$$\Delta\mu^\circ = \mu^\circ_s - \mu^\circ_w = RT\ln\gamma \qquad (8)$$

K^w_{MeOH} of methanol in water is related to a_{H^+} and a_{OMe^-} for a methanol–water mixture by equation (9) in which

$$K^w_{MeOH} = (a_{H^+}\gamma_{H^+}a_{OMe^-}\gamma_{OMe^-}/a^w_{MeOH}) = K_{MeOH}\gamma_{H^+}\gamma_{OMe^-}(a^m_{MeOH}/a^w_{MeOH}) \qquad (9)$$

a^w_{MeOH} is the molal activity of methanol referred to pure water standard state. Combination of equations (6), (7), and (9) leads to equation (10).

$$K_S = K^w_{H_2O}(a^w_{H_2O}/\gamma_{H^+}\gamma_{OH^-}) + K^w_{MeOH}(a^w_{MeOH}/\gamma_{H^+}\gamma_{OMe^-}) \qquad (10)$$

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[1] J. Koskikallio, *Suomen Kem.*, 1957, **30**, *B*, 111.

[2] R. Gaboriaud, J. Lelièvre, and R. Schaal, *Compt. rend.*, 1968, **266**, *C*, 746.

[3] M. Alfenaar and C. L. de Ligny, *Rec. Trav. chim.*, 1967, **86**, 929.

The acid ionization constants of water and methanol in water at 25 °C are given by equations (11)[4] and (12)[5]

$$pK^{w}_{H_2O} = -\log_{10} K^{w}_{H_2O} = 13{\cdot}9965 + \log_{10} 55{\cdot}509 = 15{\cdot}7409 \quad (11)$$

$$pK^{w}_{MeOH} = -\log_{10} K^{w}_{MeOH} = 15{\cdot}55 \quad (12)$$

respectively. Kayama[6] has measured activity coefficients for methanol and water in methanol–water mixtures at five temperatures. Values for $f^{w}_{H_2O}$, the activity coefficient (mole fraction concentration scale) of water referred to water standard state, and f^{m}_{MeOH}, the activity coefficient of methanol referred to methanol standard state, at 25 °C were interpolated from his results (Table 2). The chemical potential μ_{H_2O} of water in a methanol–water mixture is given by equation (13)

$$\mu_{H_2O} = \mu^{\circ}_{H_2O}(m) + RT \ln a^{w}_{H_2O} = \mu^{\circ}_{H_2O}(X) + RT \ln X_{H_2O} f^{w}_{H_2O} \quad (13)$$

in which $\mu^{\circ}_{H_2O}(m)$ and $\mu^{\circ}_{H_2O}(X)$ refer (water standard state) to the molal and mole fraction concentration scales respectively and X_{H_2O} is the mole fraction of water. For pure water $X_{H_2O} = 1$, $f^{w}_{H_2O} = 1$, $a^{w}_{H_2O}$ is given by equation (14), and therefore equation (15)

$$a^{w}_{H_2O} = 55{\cdot}509 \quad (14)$$

$$\mu^{\circ}_{H_2O} - \mu^{\circ}_{H_2O}(m) = RT \ln (55{\cdot}509) \quad (15)$$

follows. Values of $a^{w}_{H_2O}$ (Table 2) were calculated from $f^{w}_{H_2O}$ by use of equation (16) which follows from equations

$$a^{w}_{H_2O} = 55{\cdot}509 X_{H_2O} f^{w}_{H_2O} \quad (16)$$

(13) and (15).

TABLE 2

Data (25 °C) used for the evaluation of Δμ° of transfer of methoxide and hydroxide ions from water to methanol–water mixtures

MeOH/ % (w/w)	m_{H_2O}	m_{MeOH}	$f^{w}_{H_2O}$ *	f^{m}_{MeOH} *	$-\log_{10} \gamma_{H^+}$ †	$10^3\gamma_{H^+}$	$a^{w}_{H_2O}$ ‡	a^{w}_{MeOH} ‡
0	55·509	0·000	1·000	1·521	0·000	1000	55·509	0·0000
10	49·958	3·121	1·000	1·552	0·214	610·9	52·245	3·3292
20	44·407	6·242	1·002	1·522	0·488	325·1	48·768	6·8456
28·5	39·689	8·895	1·010	1·456	0·740	182·0	45·799	9·7292
50	27·755	15·605	1·074	1·226	1·470	33·88	38·161	16·102
60	22·204	18·725	1·133	1·138	1·874	13·37	34·119	19·001
70	16·653	21·846	1·211	1·067	2·233	5·848	29·073	22·098
80	11·102	24·967	1·298	1·024	2·558	2·767	22·177	25·866
90	5·551	28·088	1·386	1·004	2·706	1·968	12·694	30·596
100	0·000	31·209	1·429	1·000	1·4469	35·74	0·0000	36·497

* Interpolated from results in ref. 6. † Interpolated from results in ref. 3. ‡ Molality concentration scale.

The chemical potential μ_{MeOH} of methanol in methanol–water is given by equation (17) in which $\mu^{\circ}_{MeOH}(m)$ (water standard state) and $\mu^{\circ}_{MeOH}(X)$ (methanol standard state) refer to the molality and mole fraction concentration

$$\mu_{MeOH} = \mu^{\circ}_{MeOH}(m) + RT \ln a^{w}_{MeOH} = \mu^{\circ}_{MeOH}(X) + RT \ln X_{MeOH} f^{m}_{MeOH} \quad (17)$$

scales respectively and X_{MeOH} is the mole fraction of methanol. As the methanol concentration tends to zero ($m_{MeOH} \longrightarrow 0$), $a^{w}_{MeOH} \longrightarrow m_{MeOH}$, $f^{m}_{MeOH} \longrightarrow 1{\cdot}521$ (Table 2), X_{MeOH} is given by equation (18) and therefore

$$X_{MeOH} \longrightarrow (m_{MeOH}/55{\cdot}509) \quad (18)$$

equation (19) follows. Combination of equations (17)

$$\mu^{\circ}_{MeOH}(m) - \mu^{\circ}_{MeOH}(X) = RT \ln (1{\cdot}521/55{\cdot}509) \quad (19)$$

and (19) leads to equation (20) which enabled calculation

$$a^{w}_{MeOH} = (55{\cdot}509 X_{MeOH} f^{m}_{MeOH}/1{\cdot}521) \quad (20)$$

of a^{w}_{MeOH} (Table 2) from f^{m}_{MeOH}.

Free energies of transfer $\Delta\mu^{\circ}_{H^+}$ of the hydrogen ion from water to methanol–water mixtures quoted elsewhere [3,7-9] agree on the general form of the variation of $\Delta\mu^{\circ}_{H^+}$ with solvent composition but differ in their estimates of the absolute magnitude of $\Delta\mu^{\circ}_{H^+}$. In the present calculations γ_{H^+} [equation (8); Table 2] has been evaluated from $\Delta\mu^{\circ}_{H^+}$ values interpolated from the results of Alfenaar and de Ligny.[3]

The data in Table 2 combined with $K^{w}_{H_2O}$ [equation (11)] and K^{w}_{MeOH} [equation (12)] would enable [equation (10)] calculation of the separate contributions of the ionization of water and methanol to the apparent ionic product K_S of methanol–water mixtures if γ_{OH^-} and γ_{OMe^-} were known as a function of solvent composition. Alfenaar and de Ligny[3] deduced $\Delta\mu^{\circ}_{Cl^-}$, $\Delta\mu^{\circ}_{Br^-}$, and $\Delta\mu^{\circ}_{I^-}$ for the transfer of chloride, bromide, and iodide ions respectively from water to methanol–water. The values of Δμ° for each of the three anions closely approximate to a direct proportionality with methanol mole fraction in the range $0 < X_{MeOH} < 0{\cdot}9$. The present analysis is based on the assumption that $\Delta\mu^{\circ}_{OH^-}$ and $\Delta\mu^{\circ}_{OMe^-}$ for the transfer of hydroxide ions and methoxide ions are also linear functions of methanol mole fraction with proportionality constants k_{OH^-} and k_{OMe^-} respectively. Equations (21) and (22) follow from

$$\gamma_{OH^-} = \exp (k_{OH^-}X_{MeOH}/RT) \quad (21)$$

$$\gamma_{OMe^-} = \exp (k_{OMe^-}X_{MeOH}/RT) \quad (22)$$

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[4] H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, 1940, **36**, 973.

[5] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 1960, **82**, 795.

[6] T. Kayama, *Kagaku Kogaku*, 1962, **26**, 490.

[7] C. L. de Ligny and M. Alfenaar, *Rec. Trav. chim.*, 1965, **84**, 81.

[8] A. L. Andrews, H. P. Bennetto, D. Feakins, K. G. Lawrence, and R. P. T. Tomkins, *J. Chem. Soc.* (*A*), 1968, 1486.

[9] D. Feakins, ' Physico-Chemical Processes in Mixed Aqueous Solvents,' ed. F. Franks, Heinemann, London, 1967, p. 71.

equation (8) and on substitution in equation (10) lead to equation (23). The only unknown parameters in

$$\log_{10}\left\{\left(\frac{K_S\gamma_{H^+}}{a^w{}_{H_2O}}\right) - \left(\frac{K^w{}_{MeOH}a^w{}_{MeOH}}{a^w{}_{H_2O}}\right) \exp\left(-\frac{k_{OMe^-}X_{MeOH}}{RT}\right)\right\} = -2{\cdot}303\left(\frac{k_{OH^-}X_{MeOH}}{RT}\right) + \log_{10} K^w{}_{H_2O} \quad (23)$$

equation (23) are k_{OH^-} and k_{OMe^-}. These were determined by choosing k_{OMe^-} such that a linear plot of the left-hand side of the equation against X_{MeOH} ($0 < X_{MeOH} < 0{\cdot}9$) was obtained. Hence $k_{OMe^-} = 5759$ cal mol^{-1} and from the slope of the graph $k_{OH^-} = 6546$ cal mol^{-1}. Estimates of the increment to k_{OMe^-} or k_{OH^-} necessary to produce a significant deviation from linearity suggest that the error in the quoted values is less than *ca.* 20 kcal mol^{-1}. The observation that equation (23) can be made linear by the insertion of a particular value for k_{OMe^-} is strong support for the basic assumption made in this treatment that $\Delta\mu^\circ{}_{OH^-}$ and $\Delta\mu^\circ{}_{OMe^-}$ are approximately linear functions of X_{MeOH}.

$\Delta\mu^\circ{}_{OH^-}$ and $\Delta\mu^\circ{}_{OMe^-}$, calculated as $6546X_{MeOH}$ and $5759X_{MeOH}$ respectively ($0 < X_{MeOH} < 0{\cdot}9$), are compared in the Figure with the values of $\Delta\mu^\circ{}_{Br^-}$ and $\Delta\mu^\circ{}_{I^-}$ deduced by Alfenaar and de Ligny.[3] For pure methanol $\Delta\mu^\circ{}_{OMe^-}$ was calculated *via* equation (9) with $K^w{}_{MeOH}$ given by equation (12), $\gamma_{H^+} = 0{\cdot}03574$ (Table 2), and K_{MeOH} [equation (3)] given by equation (24) (Tables 1

$$pK_{MeOH} = 16{\cdot}708 + \log_{10}(31{\cdot}209) = 18{\cdot}202 \quad (24)$$

and 2). Equation (25) is analogous to equation (16)

$$a^m{}_{MeOH} = 31{\cdot}209X_{MeOH}/f^m{}_{MeOH} \quad (25)$$

($X_{MeOH} = 1$) and combined with equation (20) leads to equation (26). Hence (equation 11) $\log_{10}\gamma_{OMe^-}$

$$(a^w{}_{MeOH}/a^m{}_{MeOH}) = (55{\cdot}509/31{\cdot}209)1{\cdot}521 = 1{\cdot}1694 \quad (26)$$

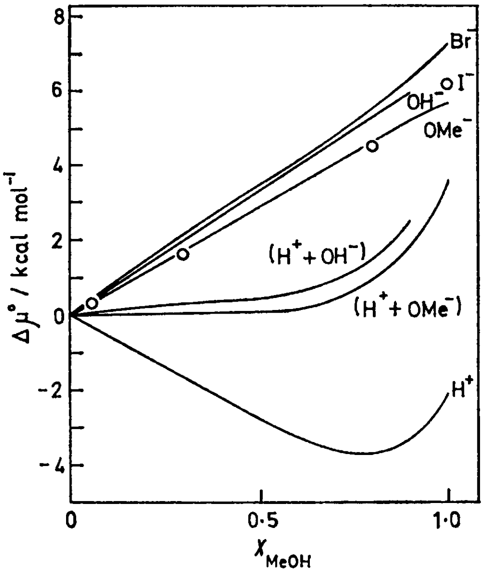
$= 4{\cdot}1672$ and $\Delta\mu^\circ{}_{OMe^-} = 5686$ cal mol^{-1} for the transfer of the methoxide ion from water to methanol.

The standard chemical potentials of transfer of ($H^+ + OH^-$) and ($H^+ + OMe^-$) are shown in the Figure and illustrate the primary medium effect on the ionic products of water and methanol respectively. For methanol the medium effect is small (<14% change in $\gamma_{H^+}\gamma_{OMe^-}$) up to *ca.* 60% (w/w) methanol. The ionic products K_w and K_m [equation (1)] of water and methanol respectively in methanol–water mixtures were evaluated from equations (27) and (28) which follow from equations

$$K_w = K^w{}_{H_2O}(a^w{}_{H_2O}/\gamma_{H^+}\gamma_{OH^-}) \quad (27)$$

$$K_m = K^w{}_{MeOH}(a^w{}_{MeOH}/\gamma_{H^+}\gamma_{OMe^-}) \quad (28)$$

(1) and (10). The figures are in Table 3 together with the calculated [equation (1)] values for K_S, the apparent ionic product of the solvent mixtures. The calculated and experimental (Table 1) K_S values are in excellent agreement (Δ, Table 3) over the complete range of solvent composition. The agreement is further support for the validity of the assumption made in this treatment that the free energies of transfer of hydroxide ions and methoxide ions from water to methanol–water mixtures are approximately linear functions of the mole fraction of methanol. Ratios of methoxide ion concentration to hydroxide ion concentration and the acid ionization constants $K_a(H_2O) = (K_w/m_{H_2O})$ and $K_a(MeOH) = (K_m/m_{MeOH})$ of water and methanol respectively in the solvent mixtures are also in Table 3. The ionization constants are referred to a standard state in the particular solvent composition to which they refer. The activities of water and methanol referred to the standard state are therefore equal to the molalities of the two components.



$\Delta\mu^0$ (Molality scale) for the transfer of some ions from water to methanol–water mixtures

Calculations have also been carried out to test whether separation of K_S into K_w and K_m was possible by use of the free energies of transfer of the proton from water to methanol–water mixtures quoted by Andrews *et al.*[8] These differ somewhat from the values (Table 2) evaluated by Alfenaar and de Ligny.[3] The corresponding free energies of transfer of the chloride, bromide, and iodide ions do not approximate to linear functions of X_{MeOH} and therefore equations (21) and (22) are unlikely to be applicable. However the free energies of transfer of the three anions are good linear functions of each other. Equations (29) and (30), in which k_{OH^-} and

$$\Delta\mu^\circ{}_{OH^-} = \tfrac{1}{3}k'{}_{OH^-}(\Delta\mu^\circ{}_{Cl^-} + \Delta\mu^\circ{}_{Br^-} + \Delta\mu^\circ{}_{I^-}) \quad (29)$$

$$\Delta\mu^\circ{}_{OMe^-} = \tfrac{1}{3}k'{}_{OMe^-}(\Delta\mu^\circ{}_{Cl^-} + \Delta\mu^\circ{}_{Br^-} + \Delta\mu^\circ{}_{I^-}) \quad (30)$$

k_{OMe^-} are proportionality constants, can be written on the assumption that the free energies of transfer of hydroxide ions and methoxide ions are similarly linear

TABLE 3

Calculated * apparent ionic products of methanol–water mixtures and ionic products and acid ionization constants of water and methanol in methanol–water mixtures at 25 °C; K_w, K_m, and K_s in mol² kg⁻²; K_a in mol kg⁻¹

MeOH/ % (w/w)	pK_w	pK_m	pK_s (calc)	Δ †	$\left(\frac{m_{OMe^-}}{m_{OH^-}}\right)$	pK_a (H_2O)	pK_a (MeOH)
0	13·997	∞	13·997	0·000	0	15·741	15·55 ‡
10	14·091	15·061	14·047	0·010	0·107	15·790	15·556
20	14·156	14·746	14·057	0·002	0·257	15·804	15·542
28·5	14·219	14·595	14·066	−0·001	0·421	15·818	15·544
50	14·416	14·392	14·103	0·006	1·06	15·860	15·585
60	14·529	14·328	14·116	−0·011	1·59	15·876	15·601
70	14·768	14·368	14·222	0·004	2·51	15·989	15·707
80	15·158	14·501	14·415	−0·008	4·54	16·204	15·898
90	15·938	14·883	14·846	0·001	12·75	16·682	16·331
100	∞	16·708	16·708	0·000	∞		18·202

* Calculations based on the results of Alfenaar and de Ligny [3] for the activity coefficient of the proton in methanol–water mixtures. † Δ = pK_s (calc) − pK_s (expt.). ‡ Ref. 5.

TABLE 4

Calculated * apparent ionic products of methanol–water mixtures and ionic products of water and methanol in methanol–water mixtures at 25 °C; K_w, K_m, and K_S in mol² kg⁻²

MeOH/% (w/w)	$-\log^{10} \gamma_{H^+}$	$\log_{10} \gamma_h$ †	pK_w	pK_m	pK_S	Δ ‡
0	0·000	0·000	13·997	∞	13·997	0·000
10	0·272	0·346	14·093	15·068	14·050	0·013
20	0·684	0·824	14·183	14·772	14·084	0·029
28·5	1·207	1·375	14·232	14·594	14·076	0·009
50	2·406	2·671	14·396	14·347	14·070	−0·027
60	2·991	3·341	14·521	14·294	14·092	−0·035
70	3·521	4·061	14·774	14·348	14·210	−0·008
80	3·952	4·776	15·166	14·493	14·409	−0·014
90	3·995	5·405	15·988	14·945	14·907	0·062
100	2·251		∞	16·708	16·708	0·000

* Calculations based on the results of Andrews *et al.*[8] for the activity coefficient of the proton in methanol–water mixtures. † Molal activity coefficients γ were interpolated from molar activity coefficients in ref. 8. ‡ Δ = pK_S (calc) − pK_S (exp.).

functions of the values for halide ions. Equations (31)

$$\log_{10} \gamma_{OH^-} = k'_{OH^-} \log_{10} \gamma_h \qquad (31)$$

and (32) follow from equation (8) and the definition of

$$\log_{10} \gamma_{OMe^-} = k'_{OMe^-} \log_{10} \gamma_h \qquad (32)$$

γ_h, equation (33). Substitution for γ_{OH^-} and γ_{OMe^-} in

$$\tfrac{1}{3}(\Delta\mu^\circ_{Cl^-} + \Delta\mu^\circ_{Br^-} + \Delta\mu^\circ_{I^-}) = RT \ln \gamma_h \qquad (33)$$

equation (10) leads to equation (34) which was solved

$$\log_{10}\left\{\left(\frac{K_S\gamma_{H^+}}{a^w{}_{H_2O}}\right) - \left(\frac{K^w{}_{MeOH}a^w{}_{MeOH}}{a^w{}_{H_2O}}\right)\gamma_h{}^{-k'_{OMe^-}}\right\} = -k'_{OH^-} \log_{10} \gamma_h + \log_{10} K^w{}_{H_2O} \qquad (34)$$

as before [equation (23)] to give 0·902 and 0·989 for k'_{OMe^-} and k'_{OH^-} respectively. The values of $\log_{10} \gamma_{H^+}$ and $\log_{10} \gamma_h$ used in the calculation are in Table 4. Hence estimates (Table 4) of K_w, K_m, and K_S were deduced *via* equations (1), (27), (28), (31), and (32).

The calculated pK_S values in Table 4 show worse agreement (Δ, Table 4) with the experimental values than do those in Table 3. However the two treatments give figures of the same order of magnitude both for K_w and for K_m. This suggests that the separation of K_S into K_w and K_m is based on a method which gives reasonable estimates of the variation of the ionic products of water and methanol with solvent composition. The values of pK_w and pK_m in Table 3 are probably the most reliable as they lead to close agreement between (K_w + K_m) and the experimentally determined apparent ionic products of the solvent mixtures.

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