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Solvation at keto-enol, acid-base and extraction equilibria and Meyer's equation

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Abstract

It is shown that the equation proposed by K. Meyer [K.H. Meyer, Berichte. 45(1912) 2843–2864] as empirical for constants of keto-enol equilibrium in various solvents is in fact a simple consequence of the additivity principle for Gibbs energies of molecules' solvation and hence is applicable to many types of chemical reactions. The examples of fulfillment of Meyer's equation in cases of keto-enol, acid-base and extraction equilibria are brought, and solvent parameters for each discussed example are determined. For the case of keto-enol equilibria with a possibility of intramolecular H-bond in enol form such parameters for 36 solvents are determined and compared with polarity parameters E_T.

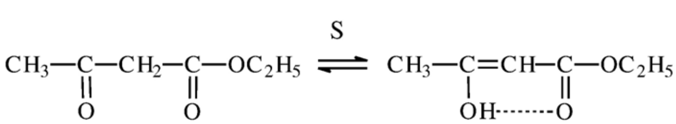
Keywords: Meyer's equation; Chemical (keto-enol, acid-base, extraction) equilibria; Solvent effects; Solvent parameters

1. Introduction

For keto-enol transitions in various solvents S

$$\text{Ket} \overset{S}{\rightleftharpoons} \text{En}$$

such as, for example,



with an equilibrium constant

$$K = [\text{En}]/[\text{Ket}]$$

K. Meyer [1,2] proposed an empirical equation

$$K_{ij} = K_{\text{st},j} E_i. \qquad (1)$$

Indexes i and j in Eq. (1) refer to keto-enols (KE) and solvents respectively. $K_{\text{st},j}$ corresponds to KE, arbitrarily chosen by Meyer as a standard, and the enolization ability E_i depends only on the nature of KE, but not on the solvent. In accordance with Eq. (1) K_{ij} is equal to the product of two multipliers, the first depending only on the reaction medium (solvent), the second only on the KE nature. At the same time standard Gibbs energy of any reaction that proceeds in a homogeneous medium (in our case $\Delta G^0_{ij} = -\text{RT}\ln K_{ij}$) always and without any assumptions can be represented [3] as a sum

$$\Delta G^0_{ij} = \Delta G^0_i(\text{vac}) + \Delta\Delta G^0_{ij}(\text{sol}), \qquad (2)$$

where the first member corresponds to the reaction proceeding in vacuum and the second represents a usual linear combination (products minus reagents) of standard Gibbs energies of solvation $\Delta G^0_{ij}(\text{sol})$ for all particles taking part in the reaction. In accordance with Eq. (2)

$$K_{ij} = K_i(\text{vac})\exp[-\Delta\Delta G^0_{ij}(\text{sol})/\text{RT}], \qquad (3)$$

where the exponential multiplier is determined by solvation of molecules and in general depends on KE as well as on the solvent in contradiction to Meyer's equation. Thus, we must explain why this exponent and the corresponding multiplier in Meyer's equation depend only on the solvent but not on KE.

O. Dimroth [4] proposed to consider Meyer's equation as a special property of a table composed from K_{ij} values. We will view

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any such the table as a matrix $\|K_{ij}\|$. If it follows Meyer's equation, all its lines are proportional to one other, as well as columns, that is

$$\begin{array}{c|c} & j \rightarrow \quad s \rightarrow \\ \hline i \downarrow \; KE & \left\| \begin{matrix} K_{11} & K_{12} & K_{13} & \cdots \\ K_{21} & K_{22} & K_{23} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{matrix} \right\| = \left\| \begin{matrix} K_{11} & K_{12} & K_{13} & \cdots \\ K_{11}E_2 & K_{12}E_2 & K_{13}E_2 & \cdots \\ K_{11}E_3 & K_{12}E_3 & K_{13}E_3 & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{matrix} \right\| = \left\| \begin{matrix} K_{11} & K_{11}B_2 & K_{11}B_3 & \cdots \\ K_{21} & K_{21}B_2 & K_{21}B_3 & \cdots \\ K_{31} & K_{31}B_2 & K_{31}B_3 & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{matrix} \right\| \end{array}$$

Here $i=1$ and $j=1$ are chosen as standards. Then:

$$K_{ij} = K_{1j}E_i, \quad E_1 = 1$$

$$K_{ij} = K_{i1}B_j, \quad B_1 = 1$$

$$K_{i1} = K_{11}E_i; \quad K_{1j} = K_{11}B_j$$

$$K_{ij} = K_{11}E_iB_j$$

In a more general case with standards $i=r$, $j=s$

$$E_r = 1, \quad B_s = 1; \quad K_{ij} = K_{rs}E_iB_j = K_{is}B_j = K_{rj}E_i$$

since $K_{is} = K_{rs}E_i; \quad K_{rj} = K_{rs}B_j$

After conversion of K_{ij} to $\log K_{ij}$ such properties of matrix $\|K_{ij}\|$ lead to the well known, but also empirical Brönsted [5,6] equation

$$\log K_{i2} = \text{const} + \log K_{i1} \tag{4}$$

for any pair of solvents and analogues equation

$$\log K_{2j} = \text{const} + \log K_{1j} \tag{5}$$

for any pair of KE's. The reverse conclusion is also true and as the Brönsted equation is known to be applicable to many chemical processes, particularly to acid-base equilibria, Meyer's equation is valid not only for keto-enol equilibria but also for all chemical systems, that follow the Brönsted equation.

Meyer's equation has not been explained theoretically up to now. M.I. Kabachnik [7] attempted to base it on the Brönsted equation for acid-base equilibria, but evidently such an approach is unsuitable. In this paper we intend to give a simple explanation of Meyer's equation and illustrate its broad applicability and usefulness by a number of examples.

2. Theory

2.1. What is the reason for Meyer's equation?

Eq. (3) in the case of keto-enol equilibrium is equivalent to

$$K_{ij} = K_i(vac)\exp[\Delta G^0_{ij}(\text{sol, Ketone}) - \Delta G^0_{ij}(\text{sol, Enol})]/\text{RT}. \tag{6}$$

It is well known [3,8] that the solvation energy of a molecule can be represented in a good approximation as an additive sum of contributions of its fragments. Therefore, what is left in the brackets of Eq. (6) is the difference

$$S_j = g_{\text{ket},j}(sol) - g_{\text{en},j}(sol), \tag{7}$$

between such contributions from functional groups of both tautomeric forms in ΔG^0_{ij}(sol). This difference evidently depends on the solvent but for a series of related KE's either does not depend or only slightly depend on the nature of a given KE, while contributions to ΔG^0_{ij}(sol) from all other parts of the molecules are being cancelled. Hence we obtain

$$K_{ij} = K_i(vac) \cdot \exp S_j/\text{RT} \tag{8}$$

as a natural basis of Meyer's equation for the keto-enol transformation, since $K_{\text{st},j} = K_{\text{st}}(\text{vac}) \exp S_j/\text{RT}$ and $K_{ij} = K_{\text{st},j}K_i(\text{vac})/K_{\text{st}}(\text{vac})$, i.e. E_i in Eq. (1) is equal to $K_i(\text{vac})/K_{\text{st}}(\text{vac})$. Now the corresponding elements of any two columns j and j' relate as $K_{ij}/K_{ij'} = \exp[S_j - S_{j'}]/\text{RT}$, and this ratio is independent of i. Thus, all properties of Meyer's matrix in the case with KE's result simply from the additivity rule for Gibbs energies of molecules' solvation. Unlike Gibbs energy of a transfer a given molecule from one solvent to another which may be called an oversolvation, one has to consider the difference S_j as the structure oversolvation in medium j due to a change of the molecule structure resulting from the tautomeric transition. The

Table 1
Solvent parameters M and E_T

NN	Solvent	Matrix A	Matrix B	[9]	E_T [10]
1	Water		−1.628	−1.55	63.1
2	Formic acid		−1.026		54.3
3	67%-methyl alcohol		−0.846		
4	Chlorbenzene			−0.83	36.8
5	Acetonitrile			−0.55	45.6
6	Nitromethane			−0.53	46.3
7	Dimethyl sulfoxide	−0.454			45.1
8	Acetic acid		−0.322		51.7
9	Methyl alcohol	−0.301	−0.276	−0.29	55.4
10	Acetone		−0.267	−0.25	42.2
11	Pyridine	−0.170			40.5
12	Methylene chloride	−0.166			40.7
13	Chloroform	−0.090	−0.214	−0.19	39.1
14	*tert*-Butyl alcohol			−0.10	43.3
15	Nitrobenzene			−0.10	41.2
16	1,4-Dioxane	−0.057		−0.21	36.0
17	Ethylene glycol			−0.03	56.3
18	Ethyl alcohol	0	0	0	51.9
19	Proryl alcohol			0	50.7
20	Ethyl acetate		−0.030	0.02	38.1
21	Isopropyl alcohol	0.077		−0.06	48.4
22	Isobutyl alcohol			0.13	47.1
23	Benzene	0.336	0.120	0.20	34.3
24	Tetrahydrofuran	0.275			37.4
25	Carbon tetrachloride	0.316		0.60	32.4
26	Toluene	0.341	0.298	0.27	33.9
27	Diethyl ether		0.416	0.43	34.5
28	Tetrachloroethylene			0.61	
29	2-Chlorbutane			0.67	
30	Carbon disulfide		0.655	0.53	32.8
31	*p*-Xylene			0.79	33.1
32	Hexane		0.856	0.79	31.1
33	Nonane			0.75	31.0
34	Cyclohexane	0.966		0.82	31.1
35	Heptane			0.97	30.9
36	Ethylbenzene			1.05	