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Determination of physical parameters of weak organic bases: hydroxamic acids

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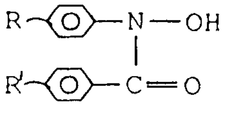
ABSTRACT: This paper presents the results of the determination of various physical parameters of *N*-aryl-substitutedhydroxamic acids. These reagents behave as weak organic bases in the presence of strongly acidic solutions. Their protonation behaviour was studied in hydrochloric acid solutions. Relevant pK_{BH^+} values were calculated according to the Hammett acidity function method, the Bunnett–Olsen method and the excess acidity method. Other physical parameters investigated were densities, molar volumes and partition data between different organic solvent–aqueous systems. An attempt was made to correlate these data with theoretical calculations based on regular solution theory and to investigate the solubility parameters of these reagents. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: weak organic bases; hydroxamic acids; physical parameters

INTRODUCTION

The versatile metal extractants *N*-aryl-substitutedhydroxamic acids, of the general formula **I**: where R and R′



I

are H, NO_2, Cl, Br or OCH_3 in *ortho, meta* or *para* positions, serve as weak organic bases in presence of strongly acidic solutions. The acid–base properties of a substance are important parameters, especially for the investigation of acid–base-catalysed reactions. The relative basicities of weak organic bases have long been of interest, both as a source of information about electronic structure and reactivities and as a means of estimating the amount of various protonated forms of a base in solutions of different acid concentrations. The most common measure of basicity has traditionally been the pK_{BH^+} of the conjugate acid of the base. Various aspects of hydroxamic acid chemistry have been reviewed.[1–3] These reagents are widely used in solvent extraction and in several other fields such as analytical, biological, agricultural, technical and nuclear investigations.[1–15] In spite of such interesting properties, the determination of the physico-chemical properties of these reagents has received little attention. In order to contribute to the solution of this problem, we report here some considerations about the protonation behaviour of *N*-aryl-substitutedhydroxamic acids. Since, as they are metal extractants, most of the studies were carried out in presence of hydrochloric acid and in the framework of our continuing research,[6,16,17] the pK_{BH^+} values of these reagents were determined following the Hammett acidity function (HAFM), Bunnett–Olsen (BOM) and excess acidity (EAM) methods in hydrochloric acid–water mixtures.

Solvent extraction is one of the most widely used separation methods, but the factors that affect the magnitude of the distribution constants are not completely understood. In chelate extraction systems, inert solvents are mainly used. Many papers have described the reaction between reagents and metal ions, but the effect of the solvent on the distribution constant has not been treated theoretically, although it constitutes one of the fundamental features of solvent extraction. With this in mind, other physical parameters such as densities, molar volumes and partition data for different organic solvent–aqueous systems were investigated. An attempt is made to correlate these partition data with theoretical calculations based on regular solution theory, which helps to determine the solubility parameters of these reagents.

EXPERIMENTAL

Instrumentation. A Spekol Model EK-1 spectro-

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photometer (Carl Zeiss, Jena, Germany) was used for the measurement of absorbance and a Varian DMS 100S UV–visible spectrophotometer was used for recording UV spectra using 10 mm matched silica cells. All calculations were carried out on a Wipro SX-386 computer under MS-DOS.

Materials. Hydroxamic acids were prepared according to the reported method[18] and purified by crystallization from benzene.

CP grade hydrochloric acid was used for extraction work, because iron(II) present in it does not interfere. Iron(II) can only affect the oxidation state of vanadium(V), which is used here as a reagent and in excess. Hence a sufficient quantity of vanadium(V) remains in the extraction system for the complete complexation of *N*-aryl-substitutedhydroxamic acids. AR grade hydrochloric acid was used for determining distribution ratios. Hydrochloric acid–water mixtures were prepared by dilution of AR grade concentrated, standardized acid with glass-distilled water.

A saturated solution of ammonium metavanadate was prepared in glass-distilled water. Before use, chloroform was shaken five or six times with an equal volume of water (to remove the ethanol present as a preservative) and distilled, then stored in amber-coloured bottle in a cool place.

Measurement of Distribution constants, K_D. An aliquot of organic solvent solution (10–15 ml) containing hydroxamic acid (*ca* 50 mg) and 25–100 ml of aqueous solution were shaken for 30 min. The volumes of the two phases to be taken were dependent on the magnitude of K_D. The solutions were allowed to stand for 1 h to accomplish phase separation at constant temperature. The concentration in each phase was determined spectrophotometrically using the vanadium(V) method.

Measurement of distribution ratio, D. To measure *D* as a function of hydrochloric acid concentration, 10 ml of organic solvent containing hydroxamic acid were equilibrated with 15–20 ml of 1–10 M hydrochloric acid for 5 min following a rapid technique.[6]

Analysis of the sample. The determination of reagent content from its UV absorbance gave unsatisfactory results because of variations in its spectral characteristics in a pure solvent and in aqueous acidic solution. The reagent concentrations were therefore determined spectrophotometrically using the vanadium(V) method.[19] This method has the advantage that side-reactions do not necessarily invalidate the measurements.

Densities of the reagents were measured by applying the hydrostatic weighing method.

All experiments were carried out in triplicate.

RESULTS AND DISCUSSION

N-Aryl-substitutedhydroxamic acids act as weak organic bases in presence of strongly acidic solutions:

$$\mathrm{HA} + \mathrm{H}^+ \overset{\mathrm{p}K_{\mathrm{BH}^+}}{\rightleftharpoons} \mathrm{H_2A}^+ \qquad (1)$$

where HA is hydroxamic acid, H_2A^+ is the conjugate acid of HA and pK_{BH^+} is the protonation constant for H_2A^+. The data summarised in Table 1, represent the pK_{BH^+} values determined, following the Hammett acidity function method (HAFM), Bunnett–Olsen method (BOM) and excess acidity method (EAM).

The HAFM[20] is suitably modified by using an acidity function appropriate to the class of bases under consideration. For each compound, pK_{BH^+} was obtained by plotting log *I* against H_0 according to the equation

$$\log I = \mathrm{p}K_{\mathrm{BH}^+} - H_0 \qquad (2)$$

where *I* = ionization ratio:

$$I = \frac{C_{\mathrm{H_2A^+}}}{C_{\mathrm{HA}}} \qquad (3)$$

C_{HA} and $C_{H_2}A^+$ being the molar concentration of hydroxamic acid and protonated species, respectively, and

$$I = \frac{K_D - D}{D} \qquad (4)$$

where K_D is the thermodynamic distribution constant of the hydroxamic acid between the organic solvent and aqueous acid in the region where appreciable protonation is occurring and is estimated by the equation

Table 1. pK_{BH^+} of *N*-aryl-substitutedhydroxamic acids by HAFM, BOM and EAM

	HAFM				BOM				EAM			
Hydroxamic acid	pK_{BH^+}	*m*	*r*	σ	pK_{BH^+}	ϕ	*r*	σ	pK_{BH^+}	*m**	*r*	σ
N-Phenyl-3,5-dinitrobenzo-	−1.83	0.90	0.990	0.10	−1.37	0.28	0.965	0.04	−2.27	1.01	0.993	0.05
N-*m*-Chlorophenylbenzo-	−2.23	1.01	0.994	0.06	−1.54	0.36	0.934	0.07	−2.65	1.27	0.992	0.08
N-*p*-Chlorophenyl-4-bromobenzo-	−2.43	1.07	0.998	0.04	−2.30	0.08	0.811	0.02	−2.99	1.35	0.997	0.05
N-*m*-Chlorophenyl-2-methoxybenzo-	−2.13	0.99	0.995	0.06	−1.99	0.11	0.794	0.03	−2.53	1.25	0.994	0.07

Table 2. Values of X as a function of hydrochloric acid concentration

	X	
HCl (M)	$-(H_A + \log C_{H^+})$	$\dfrac{-(\log I - \log C_{H^+} - pK_{BH^+})}{m^*}$
1	0.50	0.54
2	0.48	0.49
3	0.56	0.55
4	0.83	0.83
5	1.03	1.06
6	1.24	1.26
7	1.48	1.52
8	1.70	1.73
9	1.93	1.97
10	2.18	2.23

$$D = \frac{K_D - Dh_0}{K_{H_2A^+}} \tag{5}$$

(where $H_0 = -\log h_0$ $K_{H_2A^+}$ can be written as K_{BH^+} and $pK_{BH^+} = -\log K_{BH^+}$) or from the intercept of the plot of D vs Dh_0 or by calculation by the least-squares method. Because of the structural similarity of hydroxamic acids to amides, it is of interest to analyse the ionization data in terms of amide acidity function, H_A, in Eqn 2:

$$\log I = pK_{BH^+} - H_A \tag{6}$$

The second and more general method of determining pK_{BH^+} is to use the linear free energy approach originally proposed by Bunnett and Olsen,[21] provided that the plot of the left-hand side of the equation against $H_0 + \log C_{H^+}$ is linear:

$$\log I + H_0 = \phi(H_0 + \log C_{H^+}) + pK_{BH^+} \tag{7}$$

where C_{H^+} is the proton concentration and the slope ϕ is a measure of the susceptibility of the equilibrium to changing acid concentration.

The another extrapolative method is the EAM, which is an earlier approach proposed by Marziano *et al.*,[22] developed by Cox and Yates.[23] This method involves the proton concentration, C_{H^+} and the concept of excess medium acidity, X, and is summarized as

$$\log I = pK_{BH^+} + \log C_{H^+} + m^*X \tag{8}$$

where X is excess acidity. Values of X as a function of weight percentage composition are available for the aqueous hydrochloric acid system[24] and also have been calculated using the equation

$$X = -(H_A + \log C_{H^+}) \tag{9}$$

or by substituting the reported estimates of pK_{BH^+} and m^* for each base in the equation

$$X = \frac{(\log I - \log C_{H^+} - pK_{BH^+})}{m^*} \tag{10}$$

on the basis of data available for 35 conjugate acids of hydroxamic acids. The X values calculated agree very closely as shown in Table 2.

Table 1 is a summary table presenting comparative data for pK_{BH^+} determined in 4–10 M hydrochloric acid solutions by the HAFM, BOM and EAM methods, along with the values of the slope (m), correlation coefficient (r) and standard deviation (σ). Insufficient protonation at lower acidity hinders the experimental determination of pK_{BH^+}. An examination of the data reveals that for weak bases, the three different approaches give different pK_{BH^+} values. The value of pK_{BH^+} determined by EAM are the most negative among the three methods. It is interesting that the pK_{BH^+} values of structurally similar compounds, the amides, also furnished different pK_{BH^+} values with different procedures.[25] Differences in pK_{BH^+} values have been found for other weak bases also.[26] In the case of halogen substituents, the conjugate acid of *N*-*p*-chlorophenyl-4-bromobenzohydroxamic acid is a stronger base than *N*-*m*-chlorophenylbenzohydroxamic acid, whereas introduction of a methoxy group in the lower benzene ring of *N*-*m*-chlorophenylbenzohydroxamic acid in the *ortho* position further decreases the basicity of the reagent. Nitro groups are strongly electron-withdrawing oxygen-containing groups, which would be expected to interact strongly and specifically with the solvent through the formation of O—H—O type hydrogen bonds. With increasing acidity the water content decreases and so solvation decreases and the influence of substituents on the reaction centre should increase. The data presented in Table 1 show that the conjugate acid of nitro-substituted hydroxamic acid is a stronger acid than halo derivatives. Although chloro and bromo derivatives are also electron withdrawing, they would be expected to produce weaker and less specific solute–solvent interactions.

In those cases where disagreement between the three methods is observed, the question arises as to which method gives the more accurate estimate of the real thermodynamic quantity. However, it has been observed that particularly in the case of weak organic bases, HAFM works better than BOM and EAM. Further, EAM is capable of providing mechanistic information, which the other methods cannot.

Table 3 gives percentage protonation and distribution ratios, D, between an organic solvent (carbon tetrachloride) and increasing hydrochloric acid concentration (1–10 M). The percentage of protonated hydroxamic acid was calculated using the equation

$$\%\ \text{protonated} = \left(\frac{h_0}{h_0 + K_{BH^+}}\right) \times 100 \tag{11}$$

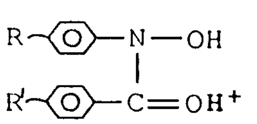
The percentage of protonated species increases and D decreases with increasing hydrochloric acid concentration. This suggests that the protonated species has a hydrophilic character.

Regarding the site of protonation of *N*-aryl-substitutedhydroxamic acids, very little information is available

Table 3. D and percentage protonation of *N*-aryl-substitutedhydroxamic acids as a function of hydrochloric acid concentration

Hydrochloric acid (M)	*N*-Phenyl-3,5-dinitrobenzo-		*N*-*m*-Chlorophenylbenzo-		*N*-*p*-Chlorophenyl-4-bromo-benzo-		*N*-*m*-Chlorophenyl-2-methoxybenzo-	
	D	% Protonation	*D*	% Protonation	*D*	% Protonation	*D*	% Protonation
1	—	4.46	—	1.83	—	1.16	—	2.29
2	52	8.15	72	3.41	640	2.18	64	4.26
3	44	13.94	65	5.91	615	3.91	60	7.51
4	35	28.48	53	13.68	565	9.09	54	16.63
5	22	44.27	45	24.02	490	16.63	45	28.47
6	14	60.77	32	38.14	405	28.00	35	43.70
7	10	75.98	25	55.73	325	41.92	26	61.31
8	7	85.48	16	70.09	235	57.34	16	74.69
9	4	91.82	10	81.70	135	71.92	8	84.90
10	3	95.72	6	89.91	80	83.63	5	91.81

in the literature.[27–29] There are two possible centres in these reagents, which can be protonated:



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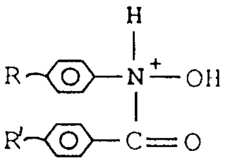
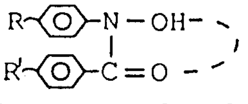
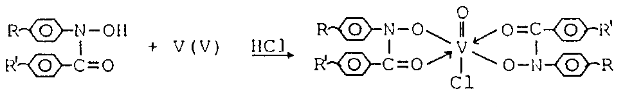


III

Of the two possibilities for a protonated species II and III, the favoured site of protonation is the carbonyl oxygen, presumably owing to its better charge delocalization into the ring and oxygen, and thus hydroxamic acids are protonated chiefly on oxygen, although at lower acidity both *O*- and *N*-protonated forms are present. At the same time, both hydroxamic acids and amides show similar protonation behaviours as they are structurally related compounds, and favour protonation at the carbonyl oxygen in the presence of strongly acidic solutions. Still, *N*-protonation is not completely impossible in amides, since *tert.* amides show an acid-catalysed isomerism, which can occur only by *N*-protonation. Further, amides with electron-donating substituents exchanged through *N*-protonation.[30] Another controversy is that, observing the IR spectra of *N*-aryl-substitutedhydroxamic acids, both $\nu_{O\text{–}H}$ and $\nu_{C=0}$ appear at lower wavelength and the positions of these bands remain unaffected on dilution. It is therefore inferred that intramolecular hydrogen bonding exists in the molecule:



Moreover, chelation occurs through both the oxygen atoms:



These two points indicate the possibilities of *N*-protonation in hydroxamic acids. The site of protonation needs very detailed studies using modern techniques of NMR spectroscopy.

N-Aryl-substitutedhydroxamic acids are versatile metal extractants. The distribution constants, K_D, of these reagents in various organic solvent–aqueous systems were determined to obtain information about the suitability of the solvent for extraction work, and these values are further helpful in calculating the solubility parameters and thus can be correlated with regular solution theory. According to Hildebrand and Scott,[31] ‘A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged’.

Hildebrand’s theory of regular solution can be applied to such solutions and the solubility parameter, δ, of a substance is defined as

$$\delta = (\delta E^{v}/v)^{1/2} \tag{12}$$

where $\delta E^{v}/v$ is the energy of vaporization per unit volume. The heat of mixing of a solute and solvents depends on the difference in their δ values. The solubility parameters of hydroxamic acids were calculated using the equation

$$\ln\left(\frac{\phi_{1,\mathrm{org}}}{\phi_{2,\mathrm{aq}}}\right) = \frac{V_1}{RT}[(\delta_c - \delta_{aq})^2 - (\delta_c - \delta_{org})^2] + V_1\left[\frac{1}{V_{org}} - \frac{1}{V_{aq}}\right] \tag{13}$$

where δ_c is the solubility parameter of solute, ϕ_1 is the volume fraction of the solute, ϕ_2 is the volume fraction of the solvent in the solution, V_1 is the molar volume of the solute, δ_{aq} is the solubility parameter of the aqueous phase, V_{aq} is the volume of the aqueous phase for all organic solvents and V_{org} is the volume of the organic solvent.

At low concentrations of the solute,

$$\phi_{aq} = \phi_{org} = 1 \tag{14}$$

Table 4. Physical parameters of N-aryl-substitutedhydroxamic acids

	N-Phenyl-3,5-dinitro-benzo-		*N*-*m*-Chlorophenyl-benzo-		*N*-*p*-Chlorophenyl-4-bromobenzo-		*N*-*m*-Chlorophenyl-2-methoxybenzo-	
Solvent	K_D	δ_C	K_D	δ_C	K_D	δ_C	K_D	δ_C
Benzene	88.50	15.03	259.00	14.87	939.13	15.17	289	14.85
Chlorobenzene	133.15	15.10	166.00	15.02	3027.03	15.20	175	15.02
o-Dichlorobenzene	66.89	15.33	103.00	15.24	4640.00	15.36	243	15.16
Toluene	92.59	14.87	140.10	15.50	1571.43	15.00	204	14.74
n-Hexane	11.00	14.32	8.31	14.31	45.00	14.57	3	14.38
Cyclohexane	15.00	14.72	10.32	14.72	55.00	14.90	6	14.75
Carbontetrachloride	38.52	14.82	66.25	14.74	651.85	14.94	55	14.76
Chloroform	142.00	15.07	248.93	14.93	6166.67	15.11	316	14.93
1,2-Dichloroethane	320.60	15.18	330.43	15.06	3400.00	15.36	803	15.05
Density (g ml^{-1})	1.1204		1.0930		1.5139		1.1649	
Molar volume (V_1)	270.430		226.440		215.734		238.208	

and for low concentrations of the solute used in the present investigation, it can be assumed that

$$\frac{\phi_{1,\mathrm{org}}}{\phi_{2,\mathrm{aq}}} = K_D \qquad (15)$$

where K_D is the experimental distribution constant. K_D can thus be related directly to the right-hand side terms of Eqn 13. The K_D values presented in Table 4 can be regarded as the distribution constant for the monomeric form of the reagent, as no significant variation in K_D with total reagent concentration occurs. At the same time, the ionization constant of these reagents in water is small and so the concentration of their anionic species in the aqueous phase is negligible.

The values of K_D for *N*-aryl-substitutedhydroxamic acids seem to depend on the solvent polarity. A log–log plot of K_D values against the dielectric constant of the organic solvents gives a parabolic relationship as shown in Fig. 1. Kamlet *et al.*[32] developed a π^* scale of 'solvent polarity' for solvent–solute interactions. A plot of log K_D against π^* values of the solvent yields a straight line, as shown in Fig. 2.

To calculate the molar volume, V_1, densities of these reagents were determined following the hydrostatic weighing method at 30 ± 1 °C. The data are presented in Table 4. The solubility parameter for water was taken as 23.4 cal$^{1/2}$ ml$^{1/2}$ and those for various organic solvents, δ, were obtained from literature;[33] the density of water was taken as 0.995670 g ml^{-1} at 30 °C. The solubility parameters in Table 4 show that the calculated values of δ_C for various solvents investigated here are reasonably constant. This indicates that the properties of hydroxamic acid solutions in these solvents are at least qualitatively similar to those postulated for regular solutions.

In a solvent extraction system, if we know the fundamental parameters of the solvent, the aqueous solutions and the solute, we shall be able to predict the behaviour of

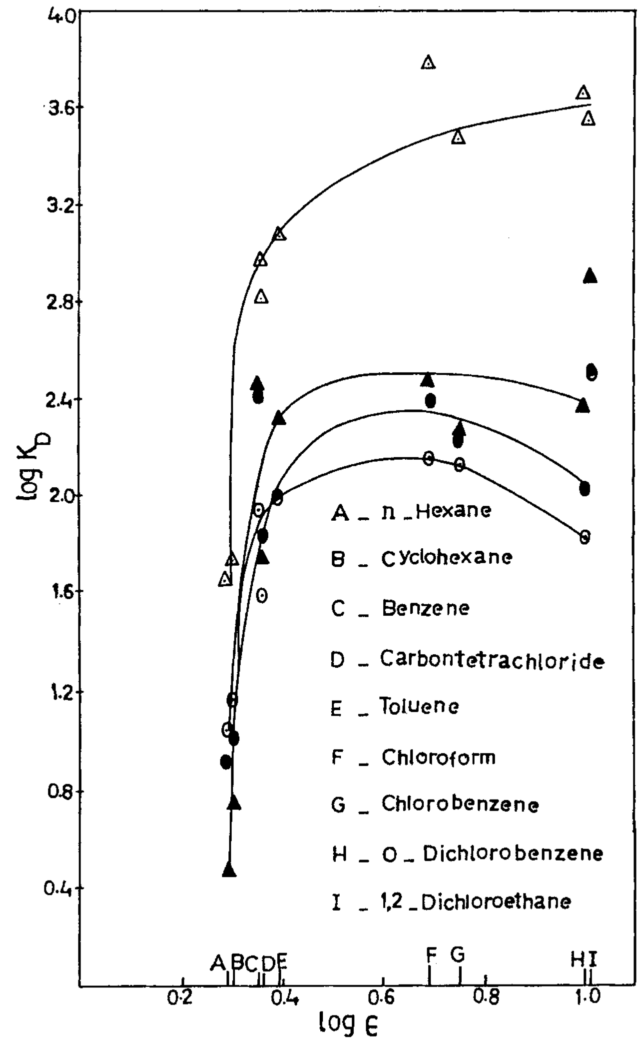


Figure 1. Log-log plot of K_D vs ϵ ⊙—⊙ *N*-phenyl-3,5-dinitrobenzo; ●—● *N*-*m*-chlorophenylbenzo; △—△ *N*-*p*-chlorophenyl-4-bromobenzo; ▲—▲ *N*-*m*-chlorophenyl-*o*-methoxy benzohydroxamic acids

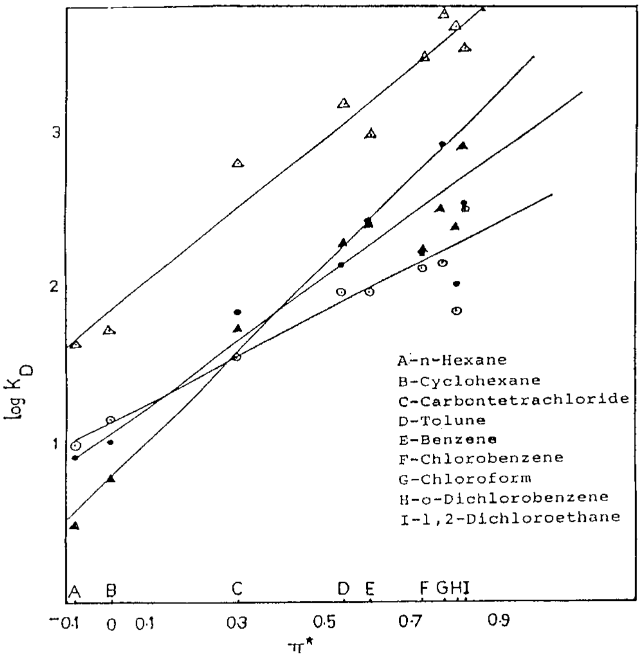


Figure 2. Plot of log K_D vs π^* ⊙—⊙ *N*-phenyl-3,5-dinitrobenzo; ●—● *N*-*m*-chlorophenylbenzo; △—△ *N*-*p*-chlorophenyl-4-bromobenzo; ▲—▲ *N*-*m*-chlorophenyl-*o*-methoxybenzo hydroxamic acids

the solute and, moreover, the role of the solvent or diluent. The knowledge of solubility parameter values will prove fruitful not only in choosing a suitable solvent for extraction but also in extending the range of the extraction method.

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