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## CHROMATOGRAPHIC STUDY OF DONOR-ACCEPTOR COMPLEXES

### ASSOCIATIONS BETWEEN ALIPHATIC AMINES OR ALCOHOLS AND TETRADENTATE $\beta$ -KETOAMINE NICKEL(II) CHELATES

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#### SUMMARY

Gas chromatography has been used to study the complexing reactions between tetradentate  $\beta$ -ketoamine (Schiff base) nickel(II) chelates and aliphatic amines or alcohols (electron donors). Using some theoretical considerations, the equilibrium constants and thermodynamic functions of the reactions where a single 1:1 complex is formed are calculated. The results are discussed in relation to the electron-donor ability of the derivatives.

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#### INTRODUCTION

The formation of complexes between electron donors and acceptors has been studied extensively. Besides spectrometric methods<sup>1</sup>, gas-liquid chromatography has been used particularly for the measurement of equilibrium constants in systems involving benzene derivatives as donors and carbon tetrabomide, trinitrobenzene or phthalate esters as acceptors<sup>2</sup>. Usually the equilibrium constants are calculated from equations generalized by Cadogan and Purnell<sup>3</sup>. However, these equations do not take into account some entropy effects resulting from mixed stationary phases and which lead to important errors in the calculation of equilibrium constants.

This study is concerned with interactions between volatile aliphatic amines or alcohols and metal chelates mixed with squalane as the inert solvent. The equations formulated by Eon *et al.*<sup>4</sup> were used and compared to the experimental results.

#### EXPERIMENTAL

The following  $\beta$ -ketoenamines and their nickel(II) chelates were prepared according to methods described earlier<sup>5,6</sup>:

TABLE I  
 PARTITION COEFFICIENTS,  $K_R$ , AND ENTHALPIES OF SOLUTION,  $\Delta H^{\circ}$  (kcal/mol), OF INVESTIGATED COMPOUNDS AT 80°C

Solute	Squalane		Ni(aaed)		Ni(aapd)		$-\Delta H_{A,S}^{\circ}$								
	$K_R$	$-\Delta H_S^{\circ}$	$K_R$	$-\Delta H_{A,S}^{\circ}$	$K_R$	$-\Delta H_{A,S}^{\circ}$									
Ethylamine	16.0	4.52	95	403	631	4.60	4.81	4.91	4.91	108	459	707	4.61	4.81	4.90
Propylamine	17.5	4.83	145	643	1011	4.94	5.20	5.30	156	682	1055	4.94	5.20	5.28	
Butylamine	18.5	4.95	157	700	1098	5.05	5.18	5.40	185	817	1265	5.10	5.36	5.50	
Pentylamine	19.0	5.24	196	889	1401	5.40	5.70	5.86	214	955	1480	5.35	5.60	5.74	
Hexylamine	19.7	5.36	232	1065	1680	5.46	5.70	5.80	253	1143	1775	5.53	5.90	6.00	
Diethylamine	16.2	4.97	106	459	719	5.05	5.25	5.30	128	552	853	5.12	5.50	5.65	
Dipropylamine	17.0	5.18	195	892	1407	5.31	5.60	5.70	201	902	1400	5.33	5.64	5.75	
Dibutylamine	18.0	5.33	250	1159	1830	5.48	5.80	5.90	239	1081	1678	5.47	5.77	5.87	
Triethylamine	19.0	6.21	301	1405	2219	6.40	6.75	6.85	317	1453	2258	6.31	6.50	6.55	
Tripropylamine	21.0	6.36	388	1824	2884	6.65	7.17	7.33	412	1900	2953	6.40	6.52	6.54	
Ethanol	10.0	3.07	11	16	20	3.20	3.58	3.78	35	127	193	3.20	3.50	3.67	
Propanol-1	12.5	3.29	18	42	60	3.35	3.74	3.90	50	191	292	3.42	3.77	4.00	
Propanol-2	13.0	3.36	81	347	544	3.68	4.50	4.85	110	481	744	3.61	4.20	4.40	
Butanol-1	40.1	3.58	285	1245	1952	3.90	4.62	4.95	354	1547	2394	4.00	5.00	5.30	
Butanol-2	50.2	3.86	365	1600	2511	3.95	4.20	4.30	470	2067	3200	3.97	4.25	4.35	
sec.-Butanol	58.3	4.17	508	2268	3567	4.30	4.60	4.72	609	2703	4190	4.30	4.57	4.70	
tert.-Butanol	62.0	4.35	589	2653	4176	4.95	6.30	6.80	704	3149	4883	4.54	5.00	5.12	

\* The mole fraction of the appropriate nickel(II) chelate in squalane solution.

<i>Systematic name</i>	<i>Abbreviation</i>
4,4'-(Ethane-1,2-diyl-diimino) bis (pent-3-en-2-one)	aaed
4,4'-(Propane-1,3-diyl-diimino) bis (pent-3-en-2-one)	aapd
[4,4'-(Ethane-1,2-diyl-diimino) bis (pent-3-en-2-onato)(2-)]nickel(II)	Ni(aaed)
[4,4'-(Propane-1,3-diyl-diimino) bis (pent-3-en-2-onato)(2-)]nickel(II)	Ni(aapd)

These compounds were characterized by elemental analysis, melting points and IR spectra in carbon tetrachloride solution. The IR spectra of the nickel(II) complexes of aaed and aapd agree with those reported<sup>6,7</sup>.

Gas chromatographic (GC) measurements were performed with a Model 504 gas chromatograph (MERA-ELWRO, Wrocław, Poland) equipped with a flame ionization detector and stainless-steel columns (2 m × 4 mm I.D.). All experiments were carried out in the temperature range 80–125 ± 0.05°C. Specially purified nitrogen was used as carrier gas. The liquid stationary phases were prepared by mixing carbon tetrachloride solutions of squalane (BDH, Poole, U.K.) and the appropriate amount of chelate. Columns were prepared from solutions of chelate in squalane having the following Ni(aaed) or Ni(aapd) mole fractions: 0.00, 0.17, 0.68 and 0.95. Chromosorb P AW DMCS (60–80 mesh) (Johns-Manville, Denver, CO, U.S.A.) was used as a support. The coating of the support by the liquid phase was about 20%.

The anhydrous aliphatic amines and alcohols, all of analytical reagent grade, were obtained from different suppliers.

Calculations were based on four individual values of the retention time for each set of solute, column and temperature.

## RESULTS AND DISCUSSION

The specific retention volumes,  $V_g$ , for each solute have been calculated from

$$V_g = j(t_R - t_M) F_o (1 - p_w/p_o) 273.16 / w_L T_o \quad (1)$$

where  $j$  denotes the compressibility factor according to James and Martin<sup>9</sup>,  $t_R$  the retention time of the solute,  $t_M$  the transit time of an inert compound (cyclohexane),  $F_o$  the volumetric flow-rate of the carrier gas at the pressure and temperature measured at the column outlet,  $T_o$  the column temperature,  $p_w$  the pressure of water vapour at this temperature,  $p_o$  the outlet pressure of the carrier gas and  $w_L$  the amount of stationary phase.

Partition coefficients,  $K_R$ , and enthalpies of solution in pure squalane,  $\Delta H_S^d$ , or in a mixture of squalane and a nickel(II) chelate,  $\Delta H_{A,S}^d$ , were calculated for each solute by the classical methods<sup>8</sup>. These characteristic data measured at 80°C on each liquid phase studied are given in Table I. The molar volume,  $v_{A,S}^o$ , of the stationary phase can be expressed as

$$v_{A,S}^o = (X_A M_A + X_S M_S) / d_{A,S} \quad (2)$$

where  $X$  and  $M$  denote the molar fraction and the molecular weight of species A and S respectively,  $d_{A,S}$  the density of the liquid phase containing the non-volatile com-

plexing agent, A, mixed with an inert solvent, S (squalane). The linear variation of  $K_R v_{A,S}^0$  with  $X_A$  for solutes giving 1:1 complexes may be expressed according to eqn. 3

$$K_R v_{A,S}^0 = K_R^0 v_S^0 [1 + (\Psi + K^*)X_A] \quad (3)$$

where  $K_R$  denotes the partition coefficient of the volatile solute, B, on the liquid phase containing the non-volatile complexing reagent, A, at the molar concentration  $X_A$ ,  $K_R^0$  the partition coefficient of solute B on the pure inert liquid phase S,  $v_S^0$  the molar volume of phase S and  $K^*$  the equilibrium constant of the complexing process between A and B. The values of  $\Psi$  were calculated from

$$\Psi + 1 = (v_A^0 / v_S^0) \cdot \exp (v_B^0/v_A^0 - v_B^0/v_S^0) \quad (4)$$

where  $v_A^0$ ,  $v_B^0$  and  $v_S^0$  are the molar volumes of the nickel(II) chelate, volatile solute B and squalane respectively. The function  $\Psi$  can be considered as constant in the narrow temperature range studied.

TABLE II

BEST-FIT REGRESSION DATA FOR THE FUNCTION  $K_R v_{A,S}^0 = f(X_A)$

$b$  = Slope;  $s_b$  = standard error of the slope,  $a$  =  $Y$  intercept;  $s_a$  = standard error of the  $Y$  intercept;  $R^2$  = correlation coefficient;  $N$  = number of determinations.

Solute	$b$	$s_b$	$a$	$s_a$	$R^2$	$N$
Ethylamine	2.4047	0.01252	8.9362	0.06035	0.9997	12
Propanol-2	2.0776	0.01643	7.2631	0.07915	0.9867	12
Propanol	0.1662	0.00833	6.7003	0.00404	0.9998	12
Ethanol	0.01843	0.00459	5.5864	0.00224	0.9989	12

Changes of  $K_R v_{A,S}^0$  with the composition of the liquid phase containing Ni(aaed) chelate were determined at 80°C for ethylamine, propanol-2, propanol-1 and ethanol. In all cases the dispersion of the experimental points is small and there is an excellent agreement between the experimental values and those calculated from the linear functions obtained by least-squares fit of the experimental results (Table II). A least-squares treatment of the data obtained yielded the equilibrium constants  $K^*$  of the association reactions at infinite dilution in squalane (see Table III). It is then possible to determine the free energies,  $\Delta G^*$ , the enthalpies,  $\Delta H^*$ , and the entropies,  $\Delta S^*$ , of the association reactions at infinite dilution in squalane:

$$\Delta G^* = RT \ln K^* \quad (5)$$

$$\ln K^* = - \frac{\Delta H^*}{R} \cdot \frac{1}{T} + \frac{\Delta S^*}{R} \quad (6)$$

The  $\Delta H^*$  and  $\Delta S^*$  values were obtained from graphs of  $\ln K^*$  vs.  $1/T$ . The data in Table III fit such linear plots very well resulting in a small standard deviation (< 7%) for  $\Delta H^*$  and  $\Delta S^*$  (Table IV).

TABLE III  
EQUILIBRIUM CONSTANTS,  $K^*$ , ENTHALPIES,  $\Delta H^*$  (kcal/mol), ENTROPIES,  $\Delta S^*$  (cal/mol.degree), AND FREE ENERGIES,  $\Delta G^*$  (kcal/mol), OF COMPLEXATION REACTIONS WITH  $\beta$ -KETOAMINE NICKEL(II) CHELATES

Solute	$Ni(aacd)$			$Ni(aapd)$		
	$K^*$	$-\Delta H^*$	$-\Delta S^*$	$K^*$	$-\Delta H^*$	$-\Delta S^*$
	*80°C		(80°C)	80°C		(80°C)
		100°C		100°C	125°C	
Ethylamine	0.57	0.53	0.49	0.90	3.66	0.39
Propylamine	0.69	0.64	0.59	0.97	3.49	0.26
Butylamine	0.69	0.65	0.62	0.95	3.41	0.25
Pentylamine	0.78	0.71	0.65	1.13	3.71	0.17
Hexylamine	0.85	0.79	0.74	0.86	2.76	0.12
Diethylamine	0.58	0.54	0.51	0.79	3.33	0.38
Dipropylamine	0.83	0.77	0.69	1.05	3.25	0.13
Dibutylamine	0.94	0.86	0.79	1.08	3.18	0.04
Triethylamine	1.07	0.98	0.89	1.14	3.09	+0.05
Tripropylamine	1.18	1.02	0.90	1.67	4.42	+0.12
Ethanol	0.31	0.25	0.21	2.41	9.15	0.82
Propanol-1	0.32	0.27	0.23	2.05	8.07	0.80
Propanol-2	0.58	0.47	0.33	3.45	10.81	0.38
Butanol-1	0.62	0.49	0.38	3.03	9.54	0.33
Butanol-2	0.63	0.58	0.54	0.95	3.62	0.32
sec.-Butanol	0.71	0.65	0.59	1.15	3.95	0.24
tert.-Butanol	0.75	0.52	0.34	4.96	14.62	0.20
				0.59	3.57	0.37
				0.70	3.41	0.25
				0.75	3.63	0.20
				0.81	2.98	0.15
				0.89	3.72	0.08
				1.23	5.32	0.32
				1.54	3.12	0.13
				1.15	3.25	0.08
				0.89	1.48	+0.07
				1.10	3.31	+0.14
				1.23	6.86	0.62
				0.41	1.84	0.59
				0.37	7.25	0.27
				0.38	11.20	0.26
				0.68	3.57	0.23
				0.49	3.42	0.17
				0.72	4.65	0.13
				0.78		
				0.83		

\* Temperature of column.

TABLE IV

BEST-FIT REGRESSION DATA FOR THE FUNCTION  $\ln K^* = f(1/T)$  OBTAINED ON COLUMNS WITH Ni(aaed) CHELATE

Parameters as in Table II.

Solute	$b$	$s_b$	$a$	$s_a$	$R^2$	$N$
Triethylamine	0.5738	0.00811	-1.5568	0.01085	0.9998	12
Dipropylamine	0.5308	0.05856	-1.6363	0.07838	0.9442	12
Butylamine	0.4810	0.00215	-1.7189	0.00288	0.9999	12
Ethylamine	0.4529	0.00239	-1.8103	0.06552	0.9998	12

As stated earlier<sup>4</sup>, a hyperbolic relationship exists between the enthalpy of solution,  $\Delta H_{A,S}^d$ , of a given solute and the mole fraction of the complexing reagent,  $X_A$ , in the inert stationary phase:

$$\Delta H_{A,S}^d = \Delta H_S^d + \Delta H^*[K^*X_A/1 + (\Psi + K^*)X_A] \quad (7)$$

This function was tested by our experimental results and a small relative error, R.S.D., less than 2%, in the difference ( $\Delta H_{A,S}^d - \Delta H_S^d$ ) has been achieved when  $X_A$  was sufficiently large ( $> 0.5$ ).

It should be pointed out that the results described above confirm the validity of the theoretical equations formulated by Eon *et al.*<sup>4</sup>. They also indicate that it does not seem possible to relate the equilibrium constant of the complexing reactions,  $K^*$ , to the molecular structures of the compounds studied. As shown in Table III, very small differences are observed between the values of  $K^*$  determined for aliphatic amines and alcohols. We can assume that rather stable associations are formed when the molecules have a localized unshared electron pair. For example, the electron pair on the nitrogen atom in ethylamine can interact with the Ni(aaed) chelate giving a  $\sigma$  complex. However, it is not possible to establish the precise structure of the complex formed.

The values shown in Table I indicate that for all the modified liquid phases the chromatographic elution order of the amines or alcohols is essentially identical to that in squalane. However, modification of the stationary phase with nickel(II) chelates considerably increased the column selectivity.

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