

Phase Equilibria in the Systems Water–Ethanol–Hydrazine Monochloride and Deuterium Oxide–Ethanol–Hydrazine Monochloride

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The phase equilibria of the systems water–ethanol–hydrazine monochloride and deuterium oxide–ethanol–hydrazine monochloride have been investigated as a function of temperature. No evidence for compound formation was found.

THE phase equilibria of the systems water–ethanol–hydrazine monochloride and deuterium oxide–ethanol–hydrazine monochloride have been investigated as functions of temperature to further an initial study of the water system at 25° and 15°C. performed by Gilbert and Humphreys (1). This study extends the upper limit of the temperature range for the water system to 65°C. The temperature range studied for the deuterium oxide system was 15° to 65°C.

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EXPERIMENTAL

Reagent grade hydrazine monochloride (K and K Laboratories) was used without further purification. Anal. Calcd. for N₂H₅Cl: Cl, 51.74%; Found: Cl, 51.56%. Reagent grade anhydrous ethanol ($n_D^{20} = 1.3598$) and conductivity water (specific conductance = 1.46×10^{-6} ohm⁻¹ cm.⁻¹) were used. Deuterium oxide (99.5% D₂O) was purchased from New England Nuclear Corp.

The samples in stoppered containers were allowed to reach equilibrium in a constant temperature bath ($\pm 0.2^\circ$ C.) for at least 2 weeks. Analysis of the chloride content of the samples and the determination of the binodal curve

Table I. Binodal Curve and Tie-Line Data

Temp., ° C.	Binodal Curve			Tie-Line Data		Temp., ° C.	Binodal Curve			Tie-Line Data			
	Wt. % ethanol	Wt. % water	Wt. % N ₂ H ₅ Cl	Wt. % N ₂ H ₅ Cl in water layer	Wt. % N ₂ H ₅ Cl in ethanol layer		Wt. % ethanol	Wt. % deuter- ium oxide	Wt. % N ₂ H ₅ Cl	Wt. % N ₂ H ₅ Cl in deuterium oxide layer	Wt. % N ₂ H ₅ Cl in ethanol layer		
45	99.54	0.00	0.46			15	58.8	32.9	8.3	40.9	16.4		
	80.3 ^a	16.0 ^a	3.7 ^a	38.4	16.9		46.5	40.0	13.5	36.5	17.6		
	63.2	27.7	9.1	45.4	11.2		29.7	46.6	23.7	38.7	15.7		
	37.8	40.1	22.1	54.4	7.3		17.1	49.3	33.6	45.3	11.2		
	28.7	43.1	28.2	43.0	14.4		6.7	46.3	47.0	44.6	11.1		
	9.7	45.5	44.8	42.7	12.4		0.5 ^c	42.1	57.4				
	4.2	38.0	57.8	36.1 ^c	14.5		0.00	38.7	61.3				
	0.00	34.8	65.2				25	62.6	29.9	7.5	35.6	16.3	
	55	99.47	0.00	0.53					49.2	38.0	12.8	34.3	16.9
		82.5	14.1	3.4	53.0			8.4	31.4	45.4	23.2	39.8	12.7
43.6		37.6	18.8	49.7 ^a	9.2	17.4		49.1	33.5	43.7	10.5		
60.6		29.0	10.4	59.0 ^a	5.8	6.5	46.4	47.1	49.7	7.8			
65	19.7	45.3	35.0	44.6	14.4	45	3.4	40.9	55.7	46.6	9.0		
	12.2	45.4	42.4	63.2	5.1		0.00	37.2	62.8				
	4.3	36.9	58.8				65	69.5	24.4	6.1	36.3	15.8	
	0.00	34.2	65.8					54.5	34.0	11.5	34.2	17.6	
	65	99.38	0.00	0.62					34.3	43.5	22.2	37.8	14.1
		70.0	22.7	7.3	45.8			11.5	18.7	48.3	33.0	41.8	11.6
		51.3	33.4	15.3	54.8		8.5	7.4	46.0	46.6	45.3	9.6	
		20.5	44.8	34.7	57.6		7.0	4.2	40.5	55.3			
	8.1 ^a	42.7 ^a	49.2 ^a	65.2 ^a	5.0 ^a		0.00	36.9	63.1				
	5.4	38.6	56.0	67.2	4.5		65	62.7	27.9	9.4	47.3	9.1	
0.00	33.9	66.1			39.7	39.9		20.4	44.4	10.9			
					21.2	46.9		31.9	41.4	12.3			
					8.1	45.7		46.2	36.3	16.5			
						5.2	40.1	54.7	37.9	14.9			
						0.00	35.6	64.4	34.2	18.6			

^a Values quoted are the average of two determinations. ^b One determination. ^c At this composition, the N₂H₅Cl crystallized out of solution rather than the two layers separating.

were carried out as described (1). The values for the binodal curve data and the tie-line data are the average of three determinations except where noted and are presented in Table I. The plait point for these systems at various temperatures was estimated as before (2). The composition of the plait point as a function of temperature is presented in Table II.

RESULTS

The data obtained in the water system at higher temperatures and in the deuterium oxide system complement the results of Gilbert and Humphreys (1), showing once again no indication of compound formation. The present study indicated that at atmospheric pressure, as suggested by Gilbert and Humphreys, there appears to be some temperature limitation for the determination of the binodal curve. In both the water system and deuterium oxide system, an upper temperature limit at ca. 67°C. is set by the start of boiling of the samples upon the addition of ethanol, and a lower temperature limit for the binodal curve is set at ca. 10.2°C. by the appearance of a solid phase (N_2H_5Cl) upon the addition of ethanol and a concomitant temperature rise in the system. Hydrazine monochloride dissolves endothermically in water.

The area under the binodal curve for the deuterium oxide systems was slightly greater than the corresponding area for the water systems at the same temperature. Judging from the trend of the binodal curves, there is no marked difference in the solubility of the salt in either water or deuterium oxide. This observation is confirmed from the experimentally determined solubilities of the salt at various temperatures.

Table II. Estimated Composition of the Plait Point

Temp., ° C.	Ethanol, Wt. %	Water, Wt. %	N_2H_5Cl , Wt. %
15 ^a	22.8	45.0	33.2
25 ^a	38.0	40.0	22.0
45	50.0	35.0	15.0
55	53.5	33.0	13.7
65	56.0	31.0	13.0
		D_2O , Wt. %	
15	48.2	39.1	12.7
25	50.7	37.3	12.0
45	50.3	36.2	13.5
65	52.5	33.7	13.8

^aTaken from the data of (1).

The plait point composition for the water system shifts towards increasing ethanol concentration with increasing temperature. The plait point composition for the deuterium oxide system shows the same general trend, although there does not seem to be as much temperature dependence.

LITERATURE CITED

- (1) Gilbert, E.C., Humphreys, L.L., *J. Chem. Eng. Data* 6, 342 (1960).
- (2) Heric, E.L., *J. Chem. Educ.* 37, 144 (1960).

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Numerical Values of the Absorbances of the Aromatic Amino Acids in Acid, Neutral, and Alkaline Solutions

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Absorbances of the aromatic amino acids have been determined at frequent wavelength intervals with the Cary M14 recording spectrophotometer in neutral and alkaline solutions. Difference spectra of acid and alkaline vs. the neutral solution were also obtained.

NUMERICAL values of the absorbances of aromatic amino acids at frequent wavelength intervals are valuable for the calculation of a spectrum corresponding to the aromatic chromophores of a protein in their free state. The choice of the free amino acids as model compounds is not the best one, because of the unknown influence of the charges present on the α -amino and the carboxyl groups, which are absent in the polypeptide chain. However, this effect may not be very large and the calculated spectra are useful as a first approximation to evaluate the spectral shifts caused by the incorporation of the chromophores into the protein fabric.

Spectra of the aromatic amino acids have been published (1, 3, 5, 7); however, it is difficult to obtain numerical

data from these, and the numerical values published are usually confined to the spectral maxima. The necessity of detailed data of this kind for the spectral study of proteins prompted their determination, and since they proved valuable, their publication appeared desirable.

MATERIALS AND METHODS

Chromatographically pure L-tyrosine, L-tryptophan, and L-phenylalanine were obtained from H. M. Chemical Co., Ltd., Santa Monica, Calif., and from Mann Research Laboratories, Inc., New York, N. Y. Fisher reagent chemical grade L-tyrosine and L-tryptophan were also used. The amino acids from all these sources were indistinguishable