Ternary Systems: Water-Acrylamide-Solvents

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Liquid-liquid and liquid-solid equilibria were determined for three different temperatures (18.5°, 25°, and 30°C) for acrylamide-water-1-butanol, acrylamide-water-2-butanone (methyl ethyl ketone), acrylamide-water-nitroethane and acrylamide-water-nitromethane. Distribution coefficients and selectivities for acrylamide between organic solvents and water were determined. Among the solvents investigated, nitromethane proved to be good for solvent extraction of acrylamide.

Ternary phase equilibrium data are very essential for solvent extraction or for salting out operations. In this study, the systems acrylamide-water-1-butanol, acrylamide-water-2-butanone, acrylamide-water-nitroethane, and acrylamide-water-nitromethane were studied at 18.5°, 25.0°, and 30.0°C.

Experimental

Materials. The solvents employed were commercial reagent grade. Acrylamide used was the Eastman Kodak White grade. Other chemicals were reagent grade. All chemicals were used without further purification.

Methods. Liquid-liquid equilibrium curve was determined by the cloud-point method (*4*). A solid-liquid equilibrium curve was determined as follows: A mixture of known composition of water and solvent was prepared and crystalline acrylamide was added slowly with shaking and keeping in a constant temperature bath. First, two immiscible liquid layers were present, and then a homogeneous phase formed. Further addition of acrylamide resulted in a saturated liquid phase and a crystalline acrylamide phase. At this point, the mixture was allowed to settle while still being held in a constant temperature bath. Then a sample of the saturated solution was analyzed for acrylamide content, and the density of the saturated solution was also determined using a specific gravity bottle. This yielded a point in the ternary diagram which lay on the solid-liquid equilibrium curve.

The line data, distribution coefficient, *K*, and selectivity, *B*, were determined as follows: The three components, in such amounts as to form two liquid phases, were prepared in a separatory funnel and shaken frequently while immersed in a constant temperature bath for 4 to 5 hr and then the mixture was allowed to settle into two layers. The two layers were separated and kept in a

Table I. Distribution Coefficient, *K*, Tie-line, and Selectivity Data for System Acrylamide-Water-1-Butanol

X_{SL}, wt. %	X_{SW}, wt. %	$K = X_{SL}/X_{SW}$	B
	at 18.5°C		
0.87	1.06	0.82	3.81
2.85	3.13	0.91	3.56
6.01	6.10	0.99	3.16
8.37	8.93	0.94	2.31
11.68	11.90	0.98	1.53
	at 25°C		
0.82	0.82	1.00	4.56
3.22	3.48	0.93	3.77
5.55	6.04	0.92	3.12
8.43	8.88	0.95	2.45
11.51	12.29	0.94	1.46
	at 30°C		
0.52	0.68	0.76	3.52
3.12	3.22	0.97	4.01
5.93	6.15	0.96	3.48
8.58	9.57	0.90	2.51
11.50	11.90	0.97	1.59

Table II. Distribution Coefficient, *K*, Tie-Line, and Selectivity Data for System Acrylamide-Water-2-Butanone (MEK)

X_{SL}, wt. %	X_{SW}, wt. %	$K = X_{SL}/X_{SW}$	B
	at 18.5°C		
0.37	0.72	0.52	2.86
2.19	3.45	0.64	2.12
3.90	4.89	0.80	2.23
	at 25°C		
0.70	0.96	0.72	4.18
2.49	3.40	0.73	2.49
3.86	3.43	0.71	2.61
	at 30°C		
0.47	0.78	0.60	3.63
2.67	3.37	0.79	2.77
3.82	4.42	0.86	2.29

Table III. Distribution Coefficient, *K*, Tie-Line, and Selectivity Data for the System Acrylamide-Water-Nitromethane

X_{SL}, wt. %	X_{SW}, wt. %	$K = X_{SL}/X_{SW}$	B
	at 18.5°C		
0.30	1.14	0.26	13.28
0.87	4.30	0.20	8.14
1.45	8.34	0.17	5.95
2.66	10.11	0.26	6.70
3.49	21.73	0.16	2.56
5.42	23.56	0.23	2.63
7.72	29.92	0.26	2.12
	at 25°C		
0.28	1.06	0.26	9.08
1.14	4.27	0.27	8.48
1.73	8.23	0.21	5.61
3.25	11.79	0.28	6.32
5.21	16.24	0.32	5.55
	at 30°C		
0.46	1.01	0.45	25.50
1.07	4.16	0.26	7.36
1.90	8.02	0.25	6.25
2.72	11.50	0.24	5.14
3.65	15.36	0.24	3.94
6.51	22.55	0.29	3.00
9.80	26.75	0.37	2.22
13.73	29.58	0.47	1.52

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constant temperature bath. The density of each layer was determined. Samples of each layer were analyzed for acrylamide content. Since these compositions must lie on the binodal curve, complete equilibrium compositions of the conjugate phases were known.

Acrylamide was determined in solution by the morpholine addition method (*2, 3*). The bromate-bromide method of determining acrylamide (*1, 3*) could not be employed because most of the solvents would interfere by getting brominated during the analysis. The plait points for liquid-liquid equilibrium curves were determined empirically on Hand's coordinates (*4*).

Accuracy of results. Temperature was maintained and measured with an accuracy of ±0.5°C. Weighings were made to 0.1 mg, using a Mettler balance. Titer values were measured to ±0.05 ml. The maximum probable error in equilibrium data is estimated to be ±1%.

Results and Discussion

Distribution coefficient, selectivity, and tie-line data are given in Tables I to IV. Figures 1 to 4 show the genera form of the results obtained. The solid-liquid equilibrium curves for the systems investigated are not simple, as one may expect for a system involving a pure solid component. Among the solvents studied, nitromethane is good for solvent extraction for acrylamide. Many more systems may have to be studied to find a good solvent.

Table IV. Distribution Coefficient, *K*, Tie-Line, and Selectivity Data for the System Acrylamide-Water-Nitroethane

X_{SL}, wt. %	X_{SW}, wt. %	$K = X_{SL}/X_{SW}$	B
	at 18.5°C		
0.37	1.38	0.27	22.80
0.48	4.90	0.98	6.72
0.97	9.22	0.11	8.38
1.26	12.20	0.10	8.70
1.56	18.05	0.09	6.64
3.20	26.78	0.12	3.90
4.24	34.12	0.13	2.64
	at 25°C		
0.26	1.30	0.20	14.90
0.74	4.00	0.15	10.80
0.82	10.09	0.08	4.94
1.64	13.48	0.12	7.20
2.98	20.08	0.15	5.89
	at 30°C		
0.19	1.01	0.19	14.70
0.65	4.90	0.13	10.40
1.42	9.56	0.15	8.50
1.69	13.14	0.13	6.83
2.23	17.88	0.12	4.14
4.10	26.72	0.15	2.85
7.07	38.37	0.18	1.75
10.38	45.49	0.23	1.26

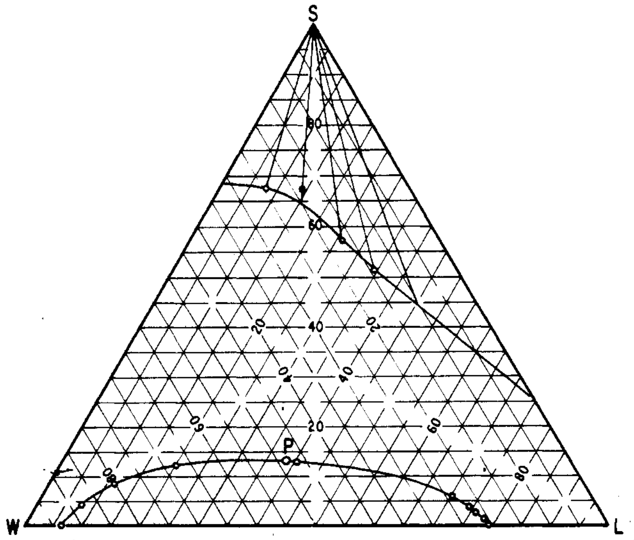

Figure 1. Phase equilibrium for system acrylamide(S)-water(W)-1-butanol(L) at 30°C

All in weight %

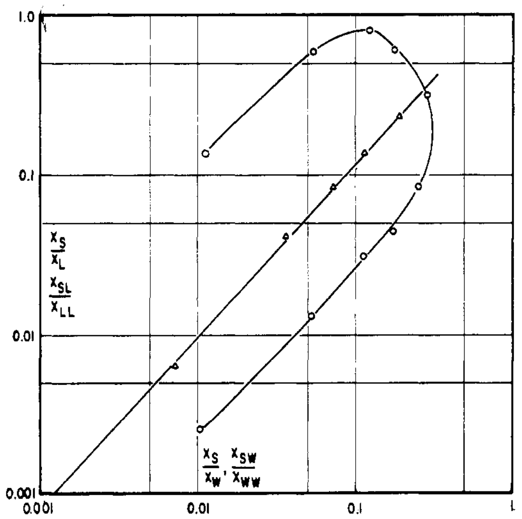

Figure 2. Plait point determination for the system acrylamide-water-1-butanol at 30°C

○ X_S/X_L vs. X_S/X_W

△ X_{SL}/X_{LL} vs. X_{SW}/X_{WW}

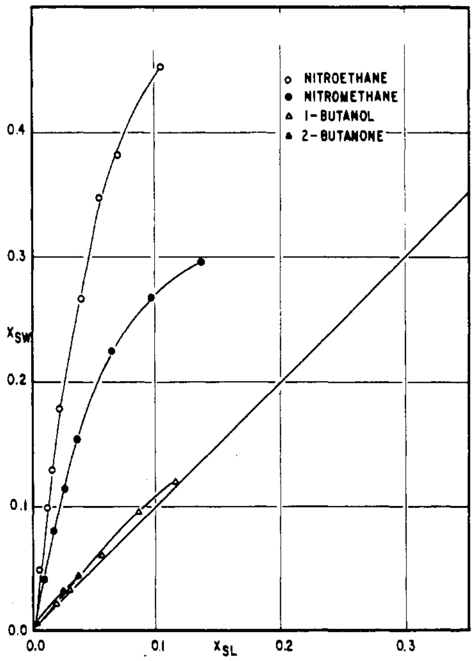

Figure 3. Distribution curve for acrylamide at 30°C

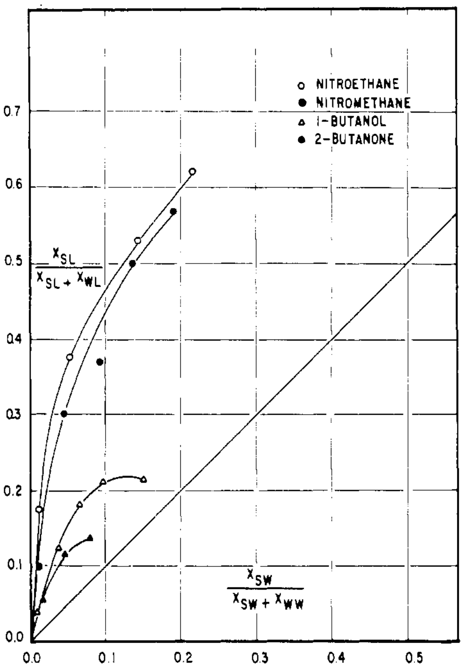

Figure 4. Selectivity curve for acrylamide at 25°C

Nomenclature

B = selectivity = $S_{SL} \cdot X_{WW}/X_{SW} \cdot X_{WL}$ = $(X_{WW}/X_{WL}) \cdot K$
K = distribution coefficient = X_{SL}/X_{SW}
X = concentration of a component in solution in weight fraction

Subscripts

L = liquid
S = solute, acrylamide
SL = solute S in solvent-rich phase L
SW = solute S in water-rich phase W
W = water
WL = water W in solvent-rich phase L
WW = water W in water-rich phase W

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Heats of Dilution of NaCl: Temperature Dependence

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The heats of dilution of aqueous NaCl were measured over a concentration range of 0.1–6.0*m* at 40°, 50°, 60°, 70°, and 80°C. The relative partial molal heat contents of solute and solvent were calculated from the experimental heats of dilution. These values were used to extend by calculation existing activity and osmotic coefficients to higher temperatures. These calculated values were found to be in excellent agreement with existing data. It is concluded that the use of heat of dilution data to correct existing values of thermodynamic quantities to higher temperatures is an efficient and very precise technique.

The thermodynamic properties of aqueous electrolyte solutions have been under investigation for many years. The subject of many of these investigations was to prove the validity of the Debye-Hückel limiting law; therefore, it is not surprising that extensive data exist for 1–1 electrolytes at 25°C *(7, 14).* In recent years aqueous electrolyte solutions have received much attention due to the interest in obtaining potable water from sea water. Most methods now under investigation for desalination of sea water involve high temperature processes. The thermodynamic behavior of aqueous electrolyte solutions must be well characterized at temperatures above 25°C in order for such processes to be both economical and efficient. However, very few precise data exist at such temperatures.

This lack of high temperature thermodynamic data is understandable in view of the experimental difficulties encountered in the direct measurement of thermodynamic parameters such as electromotive force, vapor pressure lowering, and boiling point elevation. The logical choice for obtaining high temperature data is to extend by calculation the existing thermodynamic properties at some reference temperature to the desired temperature using heat capacity data. However, this procedure is also limited. Eigen and Wicke *(4)* have measured heat capacities of a number of 1–1 aqueous electrolytes over a large temperature range. Ackermann *(1),* using the data of the above study, published apparent molal heat capacity as a function of temperature. Unfortunately, the experimental method used by Eigen and Wicke and Ackermann did not allow them to make measurements below 0.4*m* or above 2.0*m*. Therefore, the attempt to obtain the partial molal heat capacity of the solute at infinite dilution, $\bar{Cp}_2°$, by extrapolation of the ΦCp data was not accurate. Criss and Cobble *(3)* have published an extensive list of $\bar{Cp}_2°$ values over a wide temperature range obtained using the integral heat method. However, this provides only the limiting values and does not yield thermodynamic data in real concentration ranges.

The present investigation was based upon the proposition that the measurement of heats of dilution as a function of temperature and concentration is an efficient way of obtaining the desired heat capacity data. The relative apparent heat content, ΦL, which is equal to and of opposite sign to that of heat of dilution, can be related to heat capacity functions in the following manner:

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