J. Chem. Eng. Data **1997,** *42,* 1241−1243

Phase Diagrams of Aliphatic Alcohols + Magnesium Sulfate + Water

Mohammed Taghi Zafarani-Moattar* and Alireza Salabat

Physical Chemistry Department, University of Tabriz, Tabriz, Iran

Phase diagrams for aliphatic alcohols + magnesium sulfate + water were measured. The alcohols used were ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol. Phase diagram data were obtained at 25 °C, and for magnesium sulfate + ethanol + water at 25 °C and 35 °C.

Introduction

Aqueous two-phase systems formed by mixtures of two polymers, or of one polymer and one inorganic salt, are important for separation and purification of enzymes, proteins, nucleic acids, and others in biological processes (Albertsson, 1986; Vernau and Kula, 1990). This extraction technology offers the advantages of easy processing on any scale, high capacity, easy and precise scale up, and high product yields.

For large-scale processes, methods for recycling chemicals have been developed (Husledt, 1986; Greve and Kula, 1991). Greve and Kula have described the use of some two-phase systems composed of lower aliphatic alcohols + water + inorganic salts for the extraction of salt from the primary bottom phase of protein extraction processes in poly(ethylene glycol) + salt systems.

In this respect, we have studied phase diagrams of ethanol, 1-propanol, 2-propanol, 2-methyl-2-propanol + $MgSO_4$ + water systems. The binodal curve of the ethanol + $MgSO_4$ + water system at 25 °C has been determined (Tarassenkow and Katz, 1937; Jankovic, 1958), and some tie lines for this system at 50 and 75 °C have been obtained (Tarassenkow and Katz, 1937; Nikolskaya, 1946). For 2-propanol + $MgSO_4$ + water and 2-methyl-2-propanol + $MgSO_4$ + water systems only binodal curves have been determined (Ginnings and Chen, 1931; Ginnings et al., 1933). As far as we know there is no report on the phase diagram of the 1-propanol + $MgSO_4$ + water system.

In the following we describe the phase diagrams of these systems in some detail. These results can be used to develop thermodynamic models of aqueous two-phase systems (Haynes et al., 1989; Kang and Sandler, 1988; Cheluget et al., 1994).

Experimental Section

Materials. The alcohols and magnesium sulfate were obtained from Merck (2-propanol GR, min 99.7%; 1-propanol GR, min 99.5%; absolute ethanol GR, min 99.8%; *tert*-butyl alcohol GR, min 99.5%; magnesium sulfate GR, min 99.5%). All chemicals were used without further purification. The stock solutions of magnesium sulfate were made by triply distilled water, and their concentrations were ascertained by atomic absorption spectroscopy.

Apparatus and Procedure. A glass vessel, volume 50 cm^3, used to carry out the phase equilibrium determinations. It is provided with an external jacket in which water at constant temperature was circulated using a thermostat (Eyla.UA-10, Tokyo Rikakikai Co., Japan). The temperature was controlled to within ± 0.1 °C.

The binodal curves were determined by the cloud point method. A magnesium sulfate solution of known concentration was titrated with alcohol, until the solution turned turbid. The composition of the mixture was followed by mass using an analytical balance (Shimadzu 321-34553, Shimadzu Co., Japan) with a precision of $\pm 1 \times 10^{-7}$ kg.

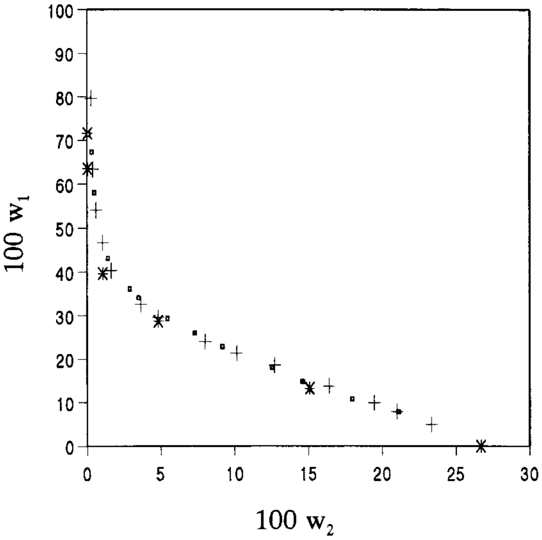

Figure 1. Comparison of binodal curves for the ethanol (1) + magnesium sulfate (2) + water (3) at 25 °C: □ present work; + Tarassenkow et al. (1937); * Jankovic (1958).

For the determination of the tie lines, feed samples (20−30 cm^3) were prepared by mixing appropriate amounts of alcohol, salt, and water in the vessel. The circulator was set at a desired temperature, and sample was stirred for 1 h. The mixture was allowed to settle for 2 h or, for some systems, overnight. Experimental apparatus were similar to the one used by Andrew et al. (1992).

After equilibrium was achieved, phases were withdrawn using syringes. The top phase was sampled first, with care being taken to leave a layer of material at least 0.5 cm thick above the interface. The bottom phase was withdrawn using a syringe with a long needle. A tiny bubble of air was retained in the needle tip and expelled once in the bottom phase to prevent contamination from upper phase material. In the cases where precipitated solid salt was present, care was taken to ensure that the sample was withdrawn gently, with the needle tip well away from salt crystals.

To analyze the upper and lower phases using the densimeter, salt and solvents must be separated from the solutions. Therefore, an evaporation apparatus similar to that devised by Yamamoto et al. (1995) was manufactured for this purpose. Approximately 10 cm^3 of phase was weighed into a glass vessel. Then water and alcohol was separated from the salt by evaporation apparatus, and the

S0021-9568(97)00060-5 CCC: $14.00

Table 1. Solubility Data as Mass Fraction for the Alcohols (1) + $MgSO_4$ (2) + Water (3)

$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$
Ethanol (25 °C)					
0.1	71.4	2.9	36.2	14.6	14.8
0.3	67.3	7.3	26.0	18.0	9.9
0.5	58.1	9.2	22.9	21.1	5.9
1.4	43.2	12.6	18.0		
1-Propanol (25 °C)					
1.2	43.4	8.4	13.9	0.27[a]	64.9
1.8	38.1	1.14[a]	43.1	23.3[b]	4.8
2.8	31.9	10.2[b]	12.4	0.12[a]	68.8
3.5	28.8	0.76[a]	54.0	28.1[b]	4.2
4.2	25.5	13.8[b]	9.1	0.05[a]	72.3
5.1	22.2	0.58[a]	57.7	29.5[b]	3.8[c]
6.6	17.9	16.3[b]	7.9		
2-Propanol (25 °C)					
2.1	35.0	11.8	14.4	2.06[a]	36.0
3.6	30.7	13.9	11.4	19.4[b]	7.0
4.3	28.6	3.30[a]	31.2	1.32[a]	37.4
5.4	26.1	15.7[b]	9.3	23.7[b]	6.5
7.1	22.7	3.23[a]	31.9	0.93[a]	39.0
10.2	17.0	17.3[b]	8.3	34.7[b]	6.3[c]
2-Methyl-2-propanol (25 °C)					
0.5	49.8	24.9	2.7	0.19[a]	64.6
1.0	43.2	1.14[a]	41.5	21.0[b]	3.2
2.1	34.5	7.0[b]	15.5	0.05[a]	70.1
4.1	24.7	0.59[a]	47.3	26.0[b]	2.0
5.2	19.9	9.9[b]	10.5	0.05[a]	77.4
11.4	8.9	0.24[a]	58.0	32.6[b]	0.9[c]
17.8	4.4	15.4[b]	5.9		
Ethanol (35 °C)					
1.1	49.3	9.6	25.3	4.92[a]	32.6
1.5	46.5	12.1	21.3	26.1[b]	11.8
3.4	38.4	16.2	16.0	4.42[a]	34.2
4.1	35.6	5.94[a]	30.7	27.0[b]	11.6
7.9	27.7	22.6[b]	13.0		

[a] Alcohol phase [b] Aqueous phase. [c] Solid $MgSO_4$ present.

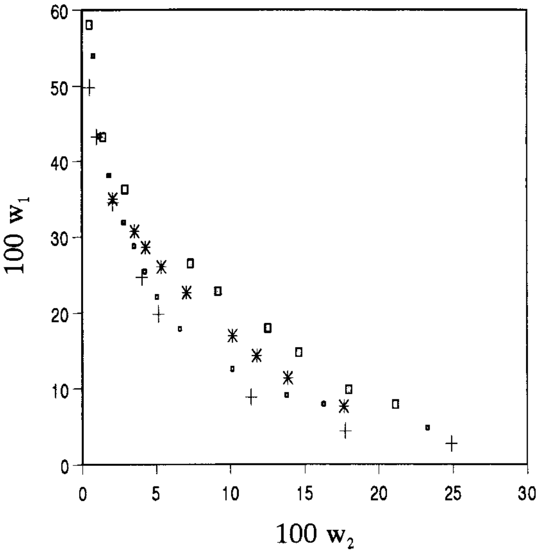

Figure 2. Binodals of alcohols (1) + magnesium sulfate (2) + water (3) at 25 °C: small □ ethanol; * 2-propanol; large □ 1-propanol; + 2-methyl-2-propanol.

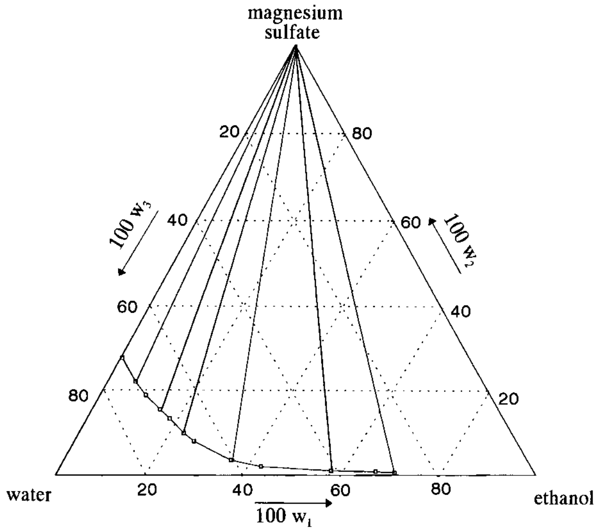

Figure 3. Phase diagram of ethanol (1) + magnesium sulfate (2) + water (3) at 25 °C.

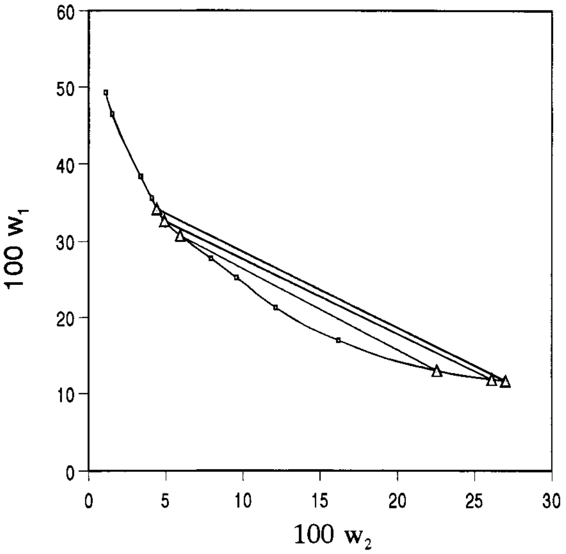

Figure 4. Phase diagram of ethanol (1) + magnesium sulfate (2) + water (3) at 35 °C.

Table 2. Plait Points

system	t/°C	$100w_2$	$100w_1$
ethanol (1) + $MgSO_4$ (2) + water (3)	35	14.7	19.5
1-propanol (1) + $MgSO_4$ (2) + water (3)	25	3.8	27.5
2-propanol (1) + $MgSO_4$ (2) + water (3)	25	7.9	21.0
2-methyl-2-propanol (1) + $MgSO_4$ (2) + water (3)	25	3.3	27.5

mass of the dried salt was determined. Mass fraction measurement of the salt by using this method was reproducible to within ±0.002 for the lower phase. Reliability of this method was tested with an atomic absorption apparatus for measuring the magnesium concentration of the upper phase. This was carried out with Shimadzu Atomic Absorption Spectrophotometer AA-670 G. The phase compositions other than salt were measured using a U-tube vibrating densimeter (Kyoto electronic DA-210). Precision of the instrument is reported to be ±0.000 01 $g{\cdot}cm^{-3}$. Calibration of the densimeter is the same as those previously described (Zafarani-Moattar et al., 1995). To obtain the mass fraction−density curves, various concentrations of each alcohol + water solution were prepared and their density values were measured at (25.0 ± 0.01) °C. The density data were fitted to the polynomial equations from which the mass fractions of alcohols were calculated with uncertainty of ±0.002. However, taking into account the corresponding error of the separation process of alcohol + water solution from the salt, for known salt + alcohol + water mixtures, the slightly higher uncertainty of ±0.003 was obtained.

Results and Discussion

The binodal curve for ethanol + magnesium sulfate + water system at 25 °C is given in Figure 1 and compared

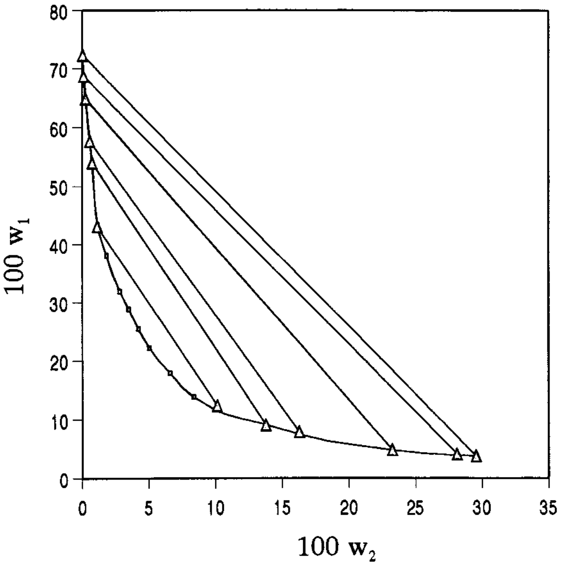

Figure 5. Phase diagram of 1-propanol (1) + magnesium sulfate (2) + water (3) at 25 °C.

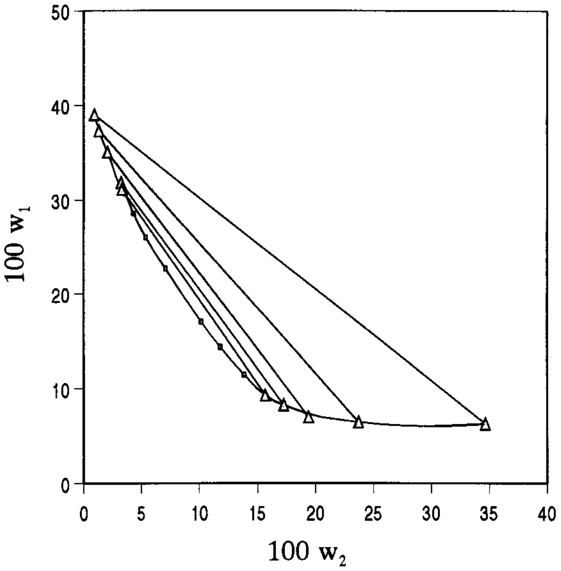

Figure 6. Phase diagram of 2-propanol (1) + magnesium sulfate (2) + water (3) at 25 °C.

with the literature. The results of the analysis and solubility data of the selected systems are given in Table 1 and are plotted in Figures 3 to 7.

The binodals of various aqueous alcohols + $MgSO_4$ systems are presented in Figure 2 at 25 °C. Reducing the number of carbon atoms in the chain from 4 to 2 improves miscibility, as expected. The effect of the higher polarity of 2-propanol as compared with that of 1-propanol is visible from the shift in the binodal (Figure 2) and from a comparison of data in Table 1.

The ternary system ethanol + $MgSO_4$ + water, however, is completely different at 25 °C (Figure 3 and Table 1). Only a solubility limit is observed, and the solution is in equilibrium with a solid phase of magnesium sulfate. On the other hand, this system forms a liquid−liquid two phase at 35 °C. In this context we studied binodal curve and tie lines for this system at 35 °C (Table 1, Figure 4).

The locations of plait points for these systems were estimated by extrapolation from the midpoints of tie lines, and the values are listed in Table 2.

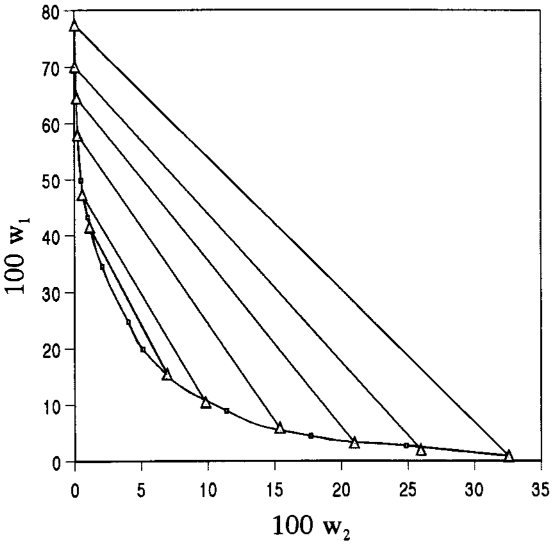

Figure 7. Phase diagram of 2-methyl-2-propanol (1) + magnesium sulfate (2) + water (3) at 25 °C.

Literature Cited

Albertsson, P. A. *Partition of Cell Particles and Macromolecules*, 3rd ed.; Wiley: New York, 1986.

Andrew, M. Ting; Lynn, S.; Prausnitz, J. M. Liquid − Liquid Equilibria for Aqueous Systems Containing *N,N*-Diethymethylamine and Sodium Chloride or Sodium Sulfate. *J. Chem. Eng. Data* **1992**, *37*, 252−259.

Cheluget, E. L.; Marx, S.; Weber, M. E.; Vera, J. H. Equilibrium in Biphasic Aqueous System: A Model for the Excess Gibbs Energy and Data for the System H_2O−NaCl-1-Propanol at 25 °C. *J. Solution Chem.* **1994**, *23*, 275−305.

Ginnings, P. M.; Chen, Z. T. Ternary Systems: Water, 2-Propanol, and Salts at 25 °C. *J. Am. Chem. Soc.* **1931**, *53*, 3765−3769.

Ginnings, P. M.; Herring, E.; Webb, B. Ternary Systems: Water, Tertiary Butanol, and Salts at 25 °C. *J. Am. Chem. Soc.* **1933**, *55*, 875−878.

Greve, A.; Kula, M. R. Recycling of salt from the primary bottom phase a protein extraction process. *J. Chem. Technol. Biotechnol.* **1991**, *50*, 27−42.

Haynes, C. A.; Beynon, R. A.; King, R. S.; Blanch, H. W.; Prausnitz, J. M. Thermodynamic Properties of Aqueous Polymer Solutions: Poly-(ethylene glycol)/Dextran. *J. Phys. Chem.* **1989**, *93*, 5612−5617.

Hustedt, H. Extractive Enzyme Recovery with Simple Recycling of Phase Forming Chemicals. *Biotechnol. Lett.* **1986**, *8*, 791−796.

Jankovic, S. Thesis, Fac. Farm., Zegreb, Yugoslavia, 1958.

Kang, C. H.; Sandler, S. I. A Thermodynamic Model for Two-Phase Aqueous Polymer Systems. *Biotechnol. Bioeng.* **1988**, *32*, 1158−1164.

Nikolskaya, A. V. The Vapor Pressure of ternary stratified systems. Aqueous alcohol solutions of potassium carbonate and magnesium sulfate. *Zh. Fiz. Khim.* **1946**, *20*, 421−431.

Tarassenkow, D. N.; Katz, K. Equilibrium in the Ternary System: Magnesium Sulfate−Ethyl alcohol−Water. *Zh. Obshch. Khim.* **1937**, *7*, 2243−2245.

Vernau, J.; Kula, M. R. Extraction of Proteins from Biological Raw Material Using Aqueous PEG/Citrate Phase systems. *Biotechnol. Appl. Biochem.* **1990**, *12*, 397−404.

Yamamoto, H.; Terano, T.; Nishi, Y.; Tokunaga, J. Vapor−Liquid Equilibria for Methanol + Ethanol + Calcium Chloride, + Ammonium Iodide, and + Sodium Iodide at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 472−477.

Zafarani-Moattar, M. T.; Salabat, A.; Kabiri-Badr, M. Volumetric Properties of PEG + SALT + WATER. *J. Chem. Eng. Data* **1995**, *40*, 559−562.

Received for review March 5, 1997. Accepted August 12, 1997.[⊗]

JE970060T

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1997.