Survey of Binary Azeotropes as Physical Chemistry Laboratory Experiments with Attention to Cost, Safety, and the Environment

Christopher W. Smith, Jason B. Cooke, and Robert J. Glinski*
Department of Chemistry, Tennessee Technological University, Cookeville, TN 38505

Investigation of the properties of a binary azeotrope is often considered a staple of the undergraduate physical chemistry laboratory (*1–3*). In the past we have studied the acetone/chloroform high-boiling system, but recently we have considered a replacement system that doesn't cause us concern over the health effects or hidden costs of waste disposal due to the use of the chlorinated solvent.

We surveyed various literature sources of azeotropic data (*4–6*) in compiling a master list of more than 80 binary systems. Initial rejections from the list were based on obviously intolerable degrees of toxicity, expense, or impracticability. Preference was given to mixtures that were commonly obtainable, miscible, and known to have convenient boiling temperatures. Table 1 presents the physical properties of our "short list" of candidate mixtures. Included in Table 1 are several unacceptable systems, which serve to illustrate our selection criteria. Currently, we are studying the low-boiling azeotrope of the water/1-propanol system. The experiment is performed on the bench top and no special precautions are required. Disposal of 1-propanol is simply by washing down the drain (*7*).

We based our final selection on several factors, including acute and chronic toxicity, boiling ranges of the components and the azeotrope, and the costs of purchase and disposal of the compounds. We sought to keep the boiling range under 100 °C because we have a set of precise (±0.1 °C) thermometers; however, thermometers that extend to 200 °C are commonly available with a precision of ±0.2 °C. Additionally, we use the refractive index to determine composition, requiring that the indices of refraction be somewhat different. Others may choose to determine composition by another method, such as gas chromatography, which allows the use of components with the same index of refraction.

Our extensive survey of azeotropic mixtures has turned up a small number of high-boiling systems. We list five of them in Table 1 and note that only two deserve serious con-

*Email: *RJG5382@TNTECH.EDU.*

Table 1. Binary Azeotropic Systems for Consideration as Physical Chemistry Laboratory Experiments

Azeotrope Component		Boiling Point/°C[a]		Flash Point/°C[b]		Exposure Limit/ppm[c]		Cost/$[d]		
A	B	A	B	A	B	A	B	A	B	Comments
					High Boiling					
Acetone	Chloroform	56	61	−9	none	1000	50	17	25	Chlorinated solvent, but preferred high boiler
Cyclohexanone	Tetrachloroethane	156	147	33	none	50	5	18	55	Chlorinated solvent, T > 100
Water	Formic acid	100	101	none	69	–	5	–	88	"Dangerously Caustic"
Water	Nitric acid	100	86	none	none	–	2	–	350	Strong oxidizing agent
Phenol	Benzaldehyde	182	179	79	64	?	5	100/kg	21/kg	"Poisonous and Toxic"
					Low Boiling					
Water	1-propanol	100	97	none	22	–	200[e]	–	28	Binary system of choice
Water	Cyclohexanol	100	161	none	63	–	50	–	13	Miscibility(?), T > 100
Water	Butyl acetate	100	126	none	23	–	200[e]	–	36	Miscibility(?), T > 100
Water	*sec*-Butanol	100	99	none	23	–	150	–	32	Immiscible
Water	1-Butanol	100	117	none	46	–	100	–	22	Miscibility(?), T > 100
Water	Toluene	100	111	none	4	–	200	–	17	Immiscible
Water	Ethanol	100	78	none	12	–	1000	–	21	Ethanol-rich azeotrope
Acetonitrile	Benzene	82	80	6	−11	40	10	32	28	Listed carcinogen
Ethanol	Benzene	78	80	12	−11	1000	10	21	28	Listed carcinogen
Ethanol	Cyclohexane	78	81	12	−20	1000	300	21	26	Flammable
Ethanol	Ethyl acetate	78	77	2	−5	1000	400	21	22	Flammable, similar RI's
Ethyl acetate	*tert*-Butanol	77	82	−5	11	400	150[e]	22	31	Flammable, similar RI's
Ethyl acetate	Cyclohexane	77	81	−5	−20	400	300	22	26	Highly flammable
Isopropanol	Ethyl acetate	82	77	12	−5	400	400	18	22	Flammable, similar RI's
Methanol	Carbon tetrachloride	64	77	16	none	200	10	17	85	Chlorinated solvent (see text)
Methanol	*n*-Heptane	64	98	16	−4	200	500	17	24	Immiscible
Methanol	Ethyl acetate	64	77	16	−5	200	400	17	22	Flammable
Methanol	Cyclohexane	64	81	16	−20	200	300	17	26	Flammable

[a]Refs *4–6*. [b]Ref *8*. [c]Threshold limit value (TLV), ref *8*, except for those marked with footnote *e*.
[d]Common supplier, catalog prices 1996. Cost is per liter, except where kilogram is specified. [e]15-minute exposure limit (STEL), ref *9*.

sideration as student experiments. The cyclohexanone/tetrachloroethane experiment is well described by Shoemaker et al. (*1*).

Our primary health concern was the exposure of the lab instructors to the chlorinated solvent for several weeks each year. We therefore listed limits of exposure to the vapor in Table 1 instead of the oral LD_{50}, since the most likely exposure in the lab is by inhalation.

Our previous use of chloroform resulted in the accumulation of about 8 liters of waste each year. This is because any amount of acetone that contains some chloroform should be treated as a chlorinated hydrocarbon and not put down the drain. Our department has cradle-to-grave accounting for “hazardous” materials, which includes a proper disposal process. Our disposal cost for these chemicals is about $30/liter, or a $240 added cost of the experiment. Other methods of disposal have been considered, such as treatment with KOH and distillation after washes with water. The KOH treatment is also costly, and the washed and distilled chloroform is not suitable for reuse in this experiment.

Finally, we note that any of the mixtures in Table 1 could be studied in a well-equipped academic lab using proper procedures. Indeed, issues regarding the proper handling of chemical waste need to be a part of the undergraduate educational experience. While we don’t feel a laboratory curriculum should be “watered down” because an experiment requires special precautions, we’re pleased to show that there are safe and “clean” alternatives that also offer high teaching value.

Literature Cited

1. Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*, 6th ed.; McGraw Hill: New York, 1996; Experiment 14.
2. Matthews, G. P. *Experimental Physical Chemistry*, Clarendon: Oxford, 1985; pp 21–79.
3. Erickson, L. E.; Morris, K. *J. Chem. Educ.* 1996, *73*, 971.
4. Perry, R. H.; Green, D. W. *Perry's Chemical Engineers' Handbook*, 6th ed. McGraw-Hill: New York, 1984, pp 13-58–13-61.
5. Horsley, L. H. *Azeotropic Data III*; American Chemical Society: Washington, DC, 1973.
6. Gmehling, J.; Omken, U. *Vapor Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt, West Germany, 1977.
7. National Research Council, *Prudent Practices for Disposal of Chemicals from Laboratories*, National Academy Press: Washington, DC, 1983.
8. *Toxic and Hazardous Industrial Chemicals Safety Manual*; International Technical Information Institute: Tokyo, Japan, 1976.
9. *The Merck Index*, 11th ed.; Budavari, S., Ed.; Merck: Rahway, NJ, 1989.