(12) Noles, J. R.; Zollweg, J. A. *Fluid Phase Equilib.* **1991**, *66*, 275.
(13) Bridgman, P. W. *The Physics of High Pressure*; G. Bell and Sons: London, 1958; p 32.
(14) Zollweg, J. A. *Thermodynamics of the Liquid Mixture Krypton + Xenon up to 190 K*; GRI Publication 91-0089; Chicago, March, 1991.
(15) Osipiuk, B.; Stryjek, R. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1970**, *18*, 289.
(16) Iglesias-Silva, G. A.; Holste, J. C.; Eubank, P. T.; Marsh, K. N.; Hall, K. R. *AIChE J.* **1987**, *33*, 1550.
(17) Prausnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1969.

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Use of Mixing Rules in Predicting Refractive Indices and Specific Refractivities for Some Binary Liquid Mixtures

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Refractive indices for the systems benzene–cyclohexane, acetone–benzene, and acetone–cyclohexane have been measured at 25 °C over the composition range. These results, combined with the corresponding densities published earlier by us, were used to test the applicability of the Lorentz–Lorenz, Gladstone–Dale, Wiener, Heller, and Arago–Biot refractive index mixing rules. The Lorentz–Lorenz relation gave the best correlation for all systems investigated. The specific refractivities for mixtures studied were also calculated.

Introduction

Experimental data of physical properties such as refractive index are required for a full understanding of the thermodynamic properties of liquid mixtures, as well as for practical chemical engineering work. Some of the important investigations, which contributed to the development of the treatment of refractive index for liquid mixtures, have been given in refs 1–3. In order to correlate the refractive index for a binary solution of a specified composition, the mixing rules of Lorentz–Lorenz, Gladstone–Dale, Wiener, Heller, and Arago–Biot are most frequently employed. Some of these relations are not suitable when there is a large change of volume on mixing, resulting from physical and/or chemical interactions. Since the constituents of the binary systems studied are of a different nature (cycloparaffin, aromatic, and ketone), their behavior in a particular mixture will be specific and depends on its composition.

In the present work the applicability of the mixing rules to calculate the refractive index data for the binary mixtures benzene–cyclohexane, acetone–benzene, and acetone–cyclohexane at 25 °C was examined.

Experimental Section

Chemicals. Analytical grade acetone, supplied by Merck, was dried over anhydrous calcium chloride (Merck) and fractionated before use. "Analar" benzene from BDH was shaken with concentrated sulfuric acid until the yellow color in the acid layer disappeared, washed with water, and dried with sodium. Finally, it was distilled twice. Only the middle cuts were used for experimental work. "RP" cyclohexane from Carlo Erba was stirred with a mixture of HNO_3 and H_2SO_4 to remove benzene, washed with NaOH solution and water, dried with sodium, and fractionated.

Table I. Comparison of Refractive Indices n_D and Densities ρ of Pure Compounds with the Selected Literature Data at 25 °C

	n_D[a]		ρ/(g cm^{-3})	
compound	exptl	lit.	exptl	lit.
acetone	1.3557	1.355 99 (*4*) 1.356 09	0.785 08	0.785 01 (*4*) 0.785 07 0.785 08
benzene	1.4978	1.497 92 (*5*)	0.873 60	0.8736 (*5a*)
cyclohexane	1.4231	1.423 54 (*5*)	0.773 86	0.773 89 (*5b*)

[a] Data apply to the sodium D-line.

Physical properties of the purified chemicals are given and compared with the selected literature data in Table I.

Measurements. Mixtures of the desired composition were prepared by weight using a Mettler H20 balance. The accuracy of the balance was 0.1 mg. The mixing cell and the procedure for preparing mixtures from liquids having different volatilities have been described previously (*6*). Refractive indices of the mixtures at the sodium D-line were measured with a Carl Zeiss Abbe refractometer, thermostated at 25 ± 0.010 °C. The precision of the measurements was ±0.0001 refractive index units.

Densities of the pure compounds and of their mixtures were measured previously (*6*, *7*) using an oscillator-type densimeter (DMA 02C Anton Paar) (*8*).

Mixing Rules. Since the mixtures are composed of constituents belonging to different classes of compounds, various molecular interactions are present. In that sense, the applicability of the most important mixing rules (suitable for predicting refractive indices in various physical situations) to the binaries under consideration has been tested.

The following mixing rules were used: the Lorentz–Lorenz equation (*9*)

$$\frac{n_{12}^2 - 1}{n_{12}^2 + 2} = \phi_1\left(\frac{n_1^2 - 1}{n_1^2 + 2}\right) + \phi_2\left(\frac{n_2^2 - 1}{n_2^2 + 2}\right) \tag{1}$$

where $\phi_i = w_i\rho_{12}/\rho_i$, $w_i = m_i/(m_1 + m_2)$, and i = 1 and 2, or in terms of specific refractivity

$$\left(\frac{n_{12}^2 - 1}{n_{12}^2 + 2}\right)\frac{1}{\rho_{12}} = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\frac{w_1}{\rho_1} + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\frac{w_2}{\rho_2} \tag{2}$$

the Wiener relation (*10*)

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$$\frac{n_{12}^2 - n_1^2}{n_{12}^2 + 2n_1^2} = \phi_2\left(\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right) \tag{3}$$

the Heller equation (*11*)

$$\frac{n_{12} - n_1}{n_1} = \frac{3}{2}\phi_2\left(\frac{m^2 - 1}{m^2 + 2}\right) \tag{4}$$

where $m = n_2/n_1$; the Gladstone–Dale equation (*12*)

$$n_{12} - 1 = \phi_1(n_1 - 1) + \phi_2(n_2 - 1) \tag{5}$$

or

$$\frac{n_{12} - 1}{\rho_{12}} = \left(\frac{n_1 - 1}{\rho_1}\right)w_1 + \left(\frac{n_2 - 1}{\rho_2}\right)w_2 \tag{6}$$

and the Arago–Biot equation (*13*)

$$n_{12} = \phi_1 n_1 + \phi_2 n_2 \tag{7}$$

The interrelations and relative merits of the above relationships, as well as the restrictions concerning their use, are given by Heller (*1*).

In order to make the calculations of refractive indices for a mixture, the following analytical expressions derived by Heller (*1*) on the basis of the above mixing rules have been used:

$$n_{12} = \left(\frac{2A + 1}{1 - A}\right)^{0.5}$$

$$A = \left[\left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\frac{1}{\rho_1} - \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\frac{w_2}{\rho_1} + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\frac{w_2}{\rho_2}\right]\rho_{12} \tag{2a}$$

(the definition equation for A given by Heller has been corrected by adding an addition sign between the second and the third term)

$$n_{12} = \left[\frac{2B(w_2\rho_{12}/\rho_2) + n_1^2}{1 - B(w_2\rho_{12}/\rho_2)}\right]^{0.5} \qquad B = \frac{n_2^2 - n_1^2}{n_2^2 + 2} \tag{2a*}$$

$$n_{12} = n_1\left(\frac{1 + 2C}{1 - C}\right)^{0.5} \qquad C = \frac{w_2\rho_{12}}{\rho_2}\left(\frac{m^2 - 1}{m^2 + 2}\right) \tag{3a*}$$

$$n_{12} = \frac{3}{2}\,\frac{w_2\rho_{12}}{\rho_2}\,\frac{m^2 - 1}{m^2 + 2}n_1 + n_1 \tag{4a*}$$

$$n_{12} = \rho_{12}\left[\frac{n_1 - 1}{\rho_1} - (n_1 - 1)\frac{w_2}{\rho_1} + (n_2 - 1)\frac{w_2}{\rho_2}\right] + 1 \tag{6a}$$

$$n_{12} = \rho_{12}\left[\frac{n_1}{\rho_1} + w_2\left(\frac{n_2}{\rho_2} - \frac{n_1}{\rho_1}\right)\right] \tag{7a}$$

$$n_{12} = (n_2 - n_1)\frac{w_2\rho_{12}}{\rho_2} + n_1 \tag{6a*, 7a*}$$

The above equations which are marked by asterisks are applicable to the mixtures with no volume change on mixing.

Results and Discussion

The experimental refractive index data for the binaries benzene–cyclohexane, acetone–benzene, and acetone–cyclohexane, observed in the present work (data for pure constituents are given, as well), and the densities determined previously (*6*, *7*) are given in Table II. Also given is the specific refractivity:

$$R_{12} = \frac{n_{12}^2 - 1}{n_{12}^2 + 2}\,\frac{1}{\rho_{12}} \tag{8}$$

Table II. Refractive Indices n_{12}, Densities ρ_{12}, Refractivities R_{12}, and Excess Volumes V^E for Mixtures at 25 °C

x_2	n_{12}	$\rho_{12}{}^a$/(g cm^{-3})	$R_{12}{}^b$/(cm^3 g^{-1})	$V^{E\,c}$/(cm^3 mol)
		Benzene (1)–Cyclohexane (2)		
1.0000	1.4231	0.773 86	0.329	0.0000
0.8979	1.4282	0.780 56	0.330	0.2494
0.7959	1.4338	0.788 02	0.330	0.4269
0.6052	1.4456	0.803 77	0.331	0.6175
0.4988	1.4530	0.813 71	0.332	0.6423
0.4021	1.4604	0.823 53	0.333	0.6124
0.2980	1.4688	0.834 96	0.333	0.5327
0.2021	1.4779	0.846 41	0.334	0.4074
0.1023	1.4873	0.859 28	0.335	0.2312
0.0000	1.4979	0.873 60	0.335	0.0000
		Acetone (1)–Benzene (2)		
1.0000	1.4979	0.873 60	0.335	0.0000
0.9456	1.4906	0.869 81	0.333	−0.0225
0.9000	1.4852	0.866 46	0.331	−0.0312
0.7938	1.4719	0.858 37	0.326	−0.0439
0.6026	1.4464	0.842 97	0.317	−0.0637
0.5018	1.4325	0.834 34	0.311	−0.0683
0.4027	1.4178	0.825 39	0.305	−0.0608
0.3022	1.4031	0.815 96	0.299	−0.0513
0.1992	1.3872	0.805 73	0.292	−0.0265
0.0990	1.3709	0.795 38	0.285	−0.0022
0.0000	1.3557	0.785 08	0.278	0.0000
		Acetone (1)–Cyclohexane (2)		
1.0000	1.4231	0.773 86	0.329	0.0000
0.8944	1.4159	0.771 09	0.325	0.4911
0.8005	1.4100	0.769 60	0.322	0.7787
0.7037	1.4036	0.768 78	0.318	0.9704
0.4970	1.3900	0.768 99	0.308	1.1208
0.3966	1.3831	0.770 12	0.303	1.0766
0.2993	1.3763	0.772 02	0.297	0.9544
0.2010	1.3693	0.774 95	0.292	0.7419
0.1024	1.3624	0.779 13	0.285	0.4317
0.0000	1.3557	0.785 08	0.278	0.0000

[a] Experimentally obtained densities (*6*, *7*). [b] Specific refractivity of mixture, calculated by eq 8. [c] Excess volume, calculated by eq 9.

This table incorporates the excess volume results (*6*, *7*), obtained according to the relation

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho_{12}} - \left(\frac{x_1}{\rho_1} + \frac{x_2}{\rho_2}\right) \tag{9}$$

The results of the predictive calculations for refractive indices, based on the mixing rules outlined in the preceding section (eqs 2a, 2a*, 3a*, 4a*, 6a, 6a*, and 7a*), are compared with the measurements in Table III. It can be seen from this table that, for all cases, the Lorentz–Lorenz mixing rule (eq 2a) was the most suitable; the Arago–Biot (eq 7a) gave in all cases poor predictions of the refractive index.

The experimental refractive index and density data were also fitted to the equations

$$n_{12} = \phi_1 n_1 + \phi_2 n_2 + \phi_1\phi_2\sum_{k=0}^{p} a_k(\phi_2 - \phi_1)^k \tag{10}$$

and

$$\rho_{12} = \phi_1\rho_1 + \phi_2\rho_2 + \phi_1\phi_2\sum_{k=0}^{p} b_k(\phi_2 - \phi_1)^k \tag{11}$$

Table III. Standard Deviations σ^a of the Experimental Data from the Predicted Results

	σ for various equations						
system	2a	2a*	3a*	4a*	6a	7a	6a*, 7a*
benzene (1)–cyclohexane (2)	0.0002	0.0028	0.0031	0.0027	0.0007	0.0042	0.0032
acetone (1)–benzene (2)	0.0004	0.0004	0.0008	0.0014	0.0015	0.0020	0.0013
acetone (1)–cyclohexane (2)	0.0004	0.0037	0.0039	0.0035	0.0007	0.0088	0.0040

[a] $\sigma = [\sum_{i=1}^{l}(n_{12,\mathrm{exptl}} - n_{12,\mathrm{calcd}})_i^2/n]^{1/2}$.

Table IV. Coefficients of Equations 10 (a_k) and 11 (b_k), Their Standard Deviations, and Standard Deviations of the Fits σ for Three Binary Systems

system	k	a_k	$\sigma(a_k)$	$b_k/(\mathrm{g\ cm^{-3}})$	$\sigma(b_k)/(\mathrm{g\ cm^{-3}})$	$\sigma(n_{12})$	$\sigma(\rho_{12})$
benzene (1)–cyclohexane (2)	0	−0.015 67	0.000 37	−0.021 08	0.000 08	0.000 15	0.000 04
	1	−0.001 84	0.000 48	−0.002 08	0.000 43		
	2	0.001 23	0.001 01	0.000 02	0.000 83		
	3			0.003 82	0.002 39		
	4			−0.001 43	0.001 32		
	5			−0.005 53	0.002 94		
acetone (1)–benzene (2)	0	−0.004 54	0.001 57	0.002 23	0.000 24	0.000 40	0.000 11
	1	0.001 56	0.001 97	0.002 72	0.000 41		
	2	−0.013 80	0.003 81				
acetone (1)–cyclohexane (2)	0	−0.021 83	0.000 77	−0.038 18	0.000 31	0.000 30	0.000 13
	1	−0.002 83	0.001 00	−0.004 31	0.000 96		
	2	−0.008 99	0.002 14	−0.004 13	0.002 58		
	3			−0.008 71	0.002 11		
	4			−0.004 41	0.004 09		

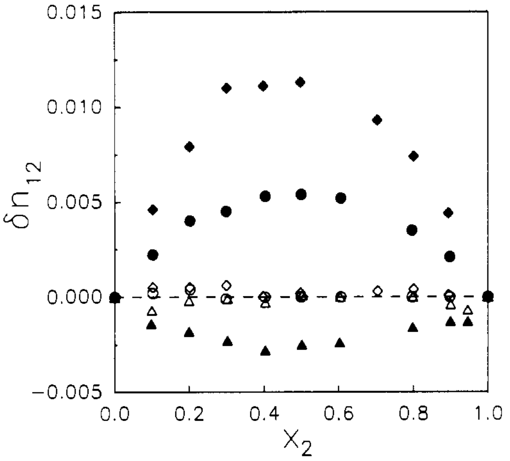

Figure 1. Dependence of difference δn_{12} on the mole fraction x_2 at 25 °C: C_6H_6 (1)–C_6H_{12} (2) (○ and ●); $(CH_3)_2CO$ (1)–C_6H_6 (2) (△ and ▲); $(CH_3)_2CO$ (1)–C_6H_{12} (2) (◇ and ◆). Empty and full symbols correspond to the n_{12} calculated by the Lorentz–Lorenz and the Arago–Biot equations, respectively.

respectively. Coefficients of these relations are presented in Table IV.

In order to illustrate the predictive abilities of various mixing rules, the deviations δn_{12} between the experimental results and the various correlations have been calculated according to

$$\delta n_{12} = n_{12,\mathrm{exptl}} - n_{12,\mathrm{calcd}} \qquad (12)$$

In this expression $n_{12,\mathrm{calcd}}$ represents the refractive index calculated according to eqs 2a, 2a*, 3a*, 4a*, 6a, 6a*, 7a, and 7a*.

Deviations δn_{12} corresponding to the Lorentz–Lorenz and to the Arago–Biot equation are presented graphically in Figure 1 for all investigated systems. The quality of the set of the other equations ranges between these two extremes. It should also be noted from this graph that the distribution of the experimental results from the Lorentz–Lorenz equation is random while there are systematic deviations from the Arago–Biot equation.

Figure 2 compares the specific refractivities based on the refractive index calculations according to the Lorentz–Lorenz and the Arago–Biot mixing rules with those calculated from the experimental data employing eq 8.

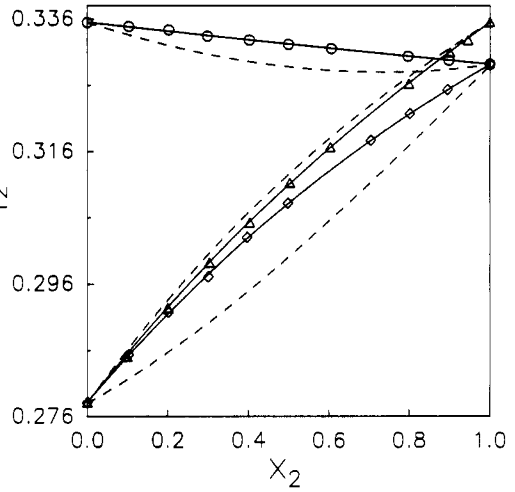

Figure 2. Dependence of specific refractivity R_{12} on mole fraction x_2 at 25 °C (data based on the experimental n_{12}): C_6H_6 (1)–C_6H_{12} (2) (○); $(CH_3)_2CO$ (1)–C_6H_6 (2) (△); $(CH_3)_2CO$ (1)–C_6H_{12} (2) (◇). Full and broken lines correspond to the predictions based on the Lorentz–Lorenz and the Arago–Biot equations, respectively.

It can be concluded from this figure that the predictions according to the Lorentz–Lorenz equation agree very well with the refractivities based on the experimental measurements. As could be expected, refractivities calculated from the Arago–Biot mixing rule are unsatisfactory except for the system acetone–benzene, for which the slightly higher values are obtained.

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Glossary

A	parameter of eq 2a
a_k	parameter of eq 10
B	parameter of eq 2a*
b_k	parameter of eq 11
C	parameter of eq 3a*
k	polynomial degree
l	number of data points

M_i	molar mass of compound i
n_i	refractive index of pure compound i for the sodium D-line
n_{12}	refractive index of the binary mixture for the sodium D-line
δn_{12}	refractive index difference defined by eq 12
R_{12}	specific refractivity of binary mixture
V^E	excess volume on mixing
x_i	mole fraction of compound i
w_2	mass fraction of compound i

Greek Letters

ρ_i	density of pure compound i
ρ_{12}	density of binary mixture
σ	standard deviation
ϕ_i	volume fraction of compound i
$\sigma(a_k)$, $\sigma(b_k)$	standard deviation of the parameters a_k and b_k, respectively
$\sigma(n_{12})$, $\sigma(\rho_{12})$	standard deviation of the fit by eqs 10 and 11, respectively

Subscripts

exptl	experimentally observed quantity
calcd	calculated quantity

Registry No. Benzene, 71-43-2; cyclohexane, 110-82-7; acetone, 67-64-1.

Literature Cited

(1) Heller, W. *J. Phys. Chem.* **1965**, *69*, 1123.
(2) Shindo, Y.; Kusano, K. *J. Chem. Eng. Data* **1979**, *24*, 106.
(3) Aminabhavi, T. M. *J. Chem. Eng. Data* **1984**, *29*, 54.
(4) Brown, I.; Foch, W. *Aust. J. Chem.* **1955**, *8*, 361.
(5) *TRC Thermodynamic Tables-Hydrocarbons*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, (a) 1985, a-3290; (b) 1986, a-2050.
(6) Radojković, N.; Tasić, A.; Djordjević, B.; Grozdanić, D. *J. Chem. Thermodyn.* **1976**, *8*, 1111.
(7) Radojković, N.; Tasić, A.; Grozdanić, D.; Djordjević, B.; Malić, D. *J. Chem. Thermodyn.* **1977**, *9*, 349.
(8) Stabinger, H.; Leopold, H.; Kratky, O. *Monatsh. Chem.* **1967**, *98*, 463.
(9) Lorentz, H. A. *Wied. Ann.* **1880**, *9*, 641. Lorenz, L. *Ibid.* **1880**, *11*, 70.
(10) Wiener, O. *Leipz. Ber.* **1910**, *62*, 256.
(11) Heller, W. *Phys. Rev.* **1945**, *68*, 5.
(12) Dale, D.; Gladstone, F. *Philos. Trans. R. Soc. London* **1858**, *148*, 887.
(13) Arago, D. F. J.; Biot, J. B. *Mem. Acad. Fr.* **1806**, 7.

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Salt Effect on Phase Equilibria by a Recirculating Still

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A new still to measure the salt effect on the vapor-liquid equilibrium at low pressures was developed. It is of the recirculating type, allowing the recirculation of both phases and the determination of its composition. The still was tested with the system ethanol-water-potassium acetate at different mole fractions of salt at 101.33 kPa.

Introduction

The most work concerning the experimental determination of the salt effect on the vapor-liquid equilibrium at low pressures uses the well-known Othmer still as standard equipment (*1-5*). Hala et al. (*6*) and Malanowski (*7*) describe one disadvantage of the Othmer still as being the superheating of the gas phase, not allowing the correct determination of the equilibrium temperature. On the other hand, only the vapor phase recirculates.

The purpose of this work was to develop, construct, and test an equilibrium still to eliminate the problems mentioned above. It differs from others which have been used for salt effect studies in the sense that both equilibrium phases recirculate with the aid of a Cottrell pump. To test the proposed apparatus, the system water-ethanol-potassium acetate was chosen. This system has been previously studied by Costa Novella and Tarrasó (*1*), Meranda and Furter (*3*), and Schmitt (*4*).

Experimental Section

Apparatus. A diagram of the apparatus is shown in Figure 1; it is a modified Naumann still (*8*) especially designed for salt effect studies in the range of 300-500 K and to 150 kPa. It is of the recirculation type, in which both liquid and vapor recirculate continuously, and allows the determination of the equilibrium composition of both phases. The essential elements are a 400 cm^3 Pyrex glass flask, 2 (equipped with a magnetic stirrer, 18, and a heating coil, 1), a Cottrell pump, 3, an equilibrium chamber, 5 (both isolated from outside by a silvered vacuum jacket, 4), a condenser, 8, for the vapor phase, a cooler, 13, for the liquid phase, two sampling ports, 10 and 14, fitted with rubber septums, and a magnetic stirred mixing chamber, 16. The volume of 400 cm^3 was chosen due to the necessity of removal of about 10 cm^3 of the liquid phase for the determination of the amount of salt in solution. Also, a large liquid volume makes possible the maintenance of a constant molar salt composition. The liquid phase return branch, 12, was built as short as possible, eliminating the occurrence of salt deposits. The equilibrium flask was involved with heating tapes to prevent heat losses.

In its operation, 350 cm^3 of solution is introduced into the still through the feed system, 20, which allows feeding also at pressures other than atmospheric. The solution is then brought partially to boil by an internal electric heater, 1. The Cottrell pump, 3, carries the mixture of liquid and vapor upward to the equilibrium chamber, 5, where the two phases, after striking directly against the thermometer stem, separate into a liquid and a vapor stream. The vapor is condensated in 8 and passed through the sampling port to the mixing chamber, 16. The liquid is cooled in 13 and passed through the sampling port, 14, to 16, where it mixes with the condensate, returning to flask 2 for recirculation.

The still can be operated at constant temperature or pressure. The steady state was usually reached after 30 min of operation. Samples of both phases are taken using syringes. Changes in composition are made by purging a known amount of solution, and replacing it by an amount of one component,

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