Table V. Computer Calculated Partial Molar Volumes of Ammonium Nitrate and Water ($\bar{V} = E + FX_{H_2O}$)

Temp (K)	$\bar{V}_{NH_4NO_3}$, cm^3 mol^{-1}	$\bar{V}_{H_2O}$, cm^3 mol^{-1}
323.2	52.29_7	18.00_3
328.2	52.46_0	18.04_8
333.2	52.54_8	18.13_1
338.2	52.69_2	18.16_8
343.2	52.81_6	18.22_1

Hence the partial molar volumes of both components, $\bar{V}_{NH_4NO_3}$ and $\bar{V}_{H_2O}$, are constant over the concentration range of ideal behavior. From this it follows that the derivatives ($\partial \bar{V}_{H_2O}/\partial X_{H_2O}$) and ($\partial \bar{V}_{NH_NO_3}/\partial X_{H_2O}$) in eq 7 would be zero. Equation 7 then reduces to

$$\left(\frac{\partial \bar{V}}{\partial X_{H_2O}}\right)_T = \bar{V}_{H_2O} - \bar{V}_{NH_4NO_3} \tag{9}$$

Partial molar volumes were evaluated by least-squares fit of molar volume and mole fraction data in eq 8; the evaluated values are given in Table V. Partial molar volumes of water at the reported temperatures are in good agreement with the molar volumes at corresponding temperatures.

The change in the molar volume could thus be found out using eq 5, which, for convenience, may be rewritten in terms of changes in molar volume with temperature ($\Delta \bar{V}_T$) and concentration ($\Delta \bar{V}_{X_{H_2O}}$)

$$d\bar{V} = \int_T^{T_0} \Delta V_T dT + \int_{x=0}^{x=x} \Delta \bar{V}_{x_{H_2O}} \, dX_{H_2O} \tag{10}$$

Using this, the effect of the two integral terms in eq 10 on the molar volume change can then be considered beyond the reference state (*16*), the effect of temperature exhibiting a decrease in ΔV_T with the increase of X_{H_2O}. The change is smooth over the range of concentration employed. $\Delta V_{X_{H_2O}}$ increases with the temperature, typical values at 323.2, 333.2, and 343.2 K being 34.28, 34.42, and 34.58 cm^3. At a given temperature $\Delta V_{X_{H_2O}}$ is reasonably constant (deviation 0.25%) confirming that NH_4NO_3–H_2O system is ideal over the range of concentration employed.

By extending the composition–molar volume isotherms (not shown in Figure 4), the *extrapolated* molar volume of NH_4NO_3 was of the same order as those evaluated from eq 8. These are, however, more than those expected at the corresponding temperatures and could arise due to unusual behavior which the system may show at $R < 1.2$.

Literature Cited

(1) Angell, C. A., *J. Electrochem. Soc.*, **112,** 1224 (1965).
(2) Braunstein, J., Orr, L., Macdonald, W., *J. Chem. Eng. Data,* **12,** 415 (1967).
(3) Campbell, A. N., Fishman, J. B., Rutherford, G., Schaffer, T. P., Ross, L., *Can. J. Chem.*, **34,** 151 (1956).
(4) "Handbook of Chemistry and Physics," 49th ed, R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio 1968, p F-5, 6.
(5) Hester, R. E., Plane, R. A., *J. Chem. Phys.*, **40,** 411 (1964).
(6) Husband, L. J. B., *J. Sci. Instrum.*, **35,** 300 (1958).
(7) Irish, D. E., Davis, A. R., *Can. J. Chem.*, **46,** 943 (1968).
(8) Keenan, A. G., *J. Phys. Chem.*, **61,** 780 (1957).
(9) MacAuley, W. J., Rhodes, E. Ubbelhode, A. R., *Proc. R. Soc. London, Ser. A,* **289,** 151 (1966).
(10) Moynihan, C. T., *J. Phys. Chem.*, **70,** 3399 (1966).
(11) Moynihan, C. T., Fratiello, A., *J. Am. Chem. Soc.*, **89,** 5546 (1967).
(12) Nikolic, R. M., Gal, I. J., *J. Chem. Soc., Dalton Trans.*, 162 (1972).
(13) Papausek, D., Kucirek, J., *Russ. J. Phys. Chem.*, **34,** 76 (1960).
(14) Peleg, M., *J. Phys. Chem.*, **75,** 2060 (1971).
(15) Péleg, M., *J. Phys. Chem.*, **75,** 3711 (1971).
(16) Spedding, P. L., *J. Electrochem. Soc.*, **117,** 177 (1970).
(17) Woessner, D. E., Snowdon, B. S., Ostroff, A. G., *J. Chem. Phys.*, **49,** 371 (1968).

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Isobaric Vapor–Liquid Equilibrium of Binary Mixtures of 1-Propanol + Chlorobenzene and 1-Butanol + Chlorobenzene

K. Venkateswara Rao,* A. Raviprasad, and C. Chiranjivi
Department of Chemical Engineering, Andhra University, Waltair, India

Vapor–liquid equilibrium data are obtained for the binary mixtures of 1-propanol–chlorobenzene and 1-butanol–chlorobenzene at atmospheric pressure. These systems show positive deviations from Raoult's law and form minimum boiling azeotropes. The experimental data are correlated satisfactorily by the three-suffix Margules equations and tested for thermodynamic consistency by the Herington test. Both the systems form symmetrical solutions.

As a part of the continuing study of phase equilibria involving alcohols, vapor–liquid equilibrium data at 760 ± 1 mmHg are measured for the two binary systems 1-propanol + chlorobenzene and 1-butanol + chlorobenzene. These systems are chosen as a part of our general study to obtain additional information on azeotropic behavior of the solutions of various organic liquids with alcohols.

Experimental Section

Purity of Chemicals. 1-Propanol, 1-butanol, and chlorobenzene (all Analytical Grade) are further purified by distilling in a laboratory packed distillation column. The physical properties of the chemicals are given in Table I. These values compare well with the values given in literature (*7*).

Analytical Method. Vapor and liquid samples are analyzed at 30 °C by means of refractive index using an Abbe's refractometer with an accuracy of ±0.0005. The composition of the vapor and liquid samples for each system is determined from the standard plot of refractive index vs. composition prepared from samples of known composition. The boiling temperatures are measured using a standard mercury-in-glass thermometer having an accuracy of ±0.1 °C.

Equilibrium Still. The equilibrium still used for determining the vapor–liquid equilibrium data is of the vapor recirculatory type of Jones, Schoenborn, and Colburn, as modified by Ward (*6*).

Table I. Physical Properties of Chemicals

	Refractive index at 25 °C		Boiling point, °C	
	Exptl	Lit.	Exptl	Lit.
1-Propanol	1.3835	1.3835	97.2	97.15
1-Butanol	1.3970	1.3972[a]	117.7	117.72
Chlorobenzene	1.5220	1.5221[a]	131.6	131.687

[a] Computed using d*n*/d*t*.

Table II. Experimental Data (System, 1-Propanol–Chlorobenzene; Pressure, 760 ± 1 mmHg)

No.	Temp, °C	x_1	y_1	γ_1	γ_2
1	117.0	0.076	0.384	2.5474	0.9970
2	113.6	0.106	0.455	2.4149	1.0055
3	111.8	0.128	0.494	2.3046	1.0096
4	106.8	0.196	0.594	2.1429	1.0213
5	104.3	0.252	0.632	1.9270	1.0743
6	103.2	0.297	0.666	1.7905	1.0694
7	101.3	0.388	0.698	1.5362	1.1833
8	100.8	0.435	0.707	1.4183	1.2638
9	100.3	0.475	0.722	1.3504	1.3110
10	98.4	0.533	0.742	1.3257	1.4533
11	97.2	0.691	0.794	1.1435	1.8240
12	96.8	0.732	0.811	1.1193	1.9546
13	96.6	0.782	0.836	1.0880	2.0987
14	96.2	0.814	0.854	1.0838	2.2190
15	96.1	0.851	0.878	1.0700	2.3223
16	95.9	0.933	0.933	1.0477	2.7272
17	96.1	0.954	0.954	1.0368	2.8362

Table III. Experimental Data (System, 1-Butanol–Chlorobenzene; Pressure, 760 ± 1 mmHg)

No.	Temp, °C	x_1	y_1	γ_1	γ_2
1	128.4	0.040	0.136	2.3755	0.9814
2	125.1	0.090	0.249	2.1470	0.9839
3	123.0	0.148	0.337	1.8913	0.9827
4	120.6	0.186	0.370	1.7877	1.0445
5	119.1	0.232	0.425	1.7295	1.0548
6	117.9	0.289	0.468	1.5916	1.0903
7	117.2	0.337	0.498	1.4873	1.1256
8	116.9	0.394	0.530	1.3680	1.1655
9	116.5	0.420	0.552	1.3548	1.1714
10	115.5	0.538	0.612	1.2133	1.3050
11	115.3	0.612	0.644	1.1303	1.4406
12	115.1	0.652	0.672	1.1146	1.4879
13	115.2	0.760	0.744	1.0552	1.6788
14	115.3	0.779	0.756	1.0273	1.7334
15	115.8	0.855	0.821	1.0137	1.9106
16	116.0	0.872	0.837	1.0063	1.9597
17	116.2	0.902	0.868	1.0021	2.0605
18	116.2	0.928	0.902	1.0122	2.0822
19	116.6	0.962	0.944	1.0079	2.2282

Results

Equilibrium vapor-liquid compositions, determined in this investigation, are reported in Tables II and III along with the activity coefficient data calculated from the experimental results. The *x*–*y* plots are presented in Figures 1 and 2 while the *T*–*x*–*y* plots are shown in Figures 3 and 4, and the log γ vs. *x* plots are given in Figures 5 and 6, respectively for the two-system 1-propanol + chlorobenzene and 1-butanol + chlorobenzene.

The activity coefficients for the two components in each system are evaluated using the equation

$$\gamma = ZPy/p^0x$$

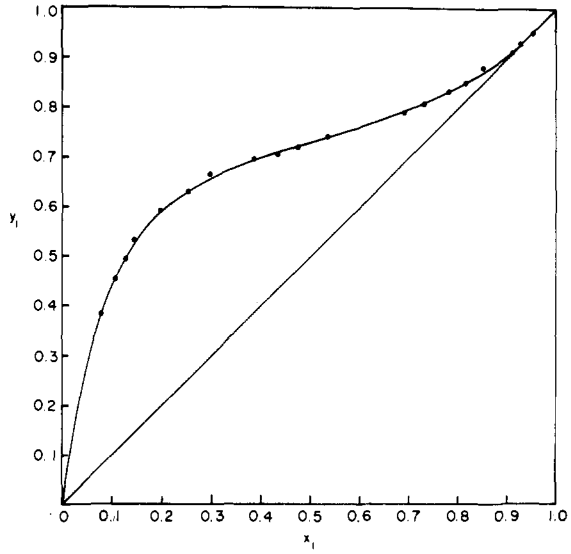

Figure 1. Equilibrium curve for the 1-propanol–chlorobenzene system: ●, experimental; —, theoretical.

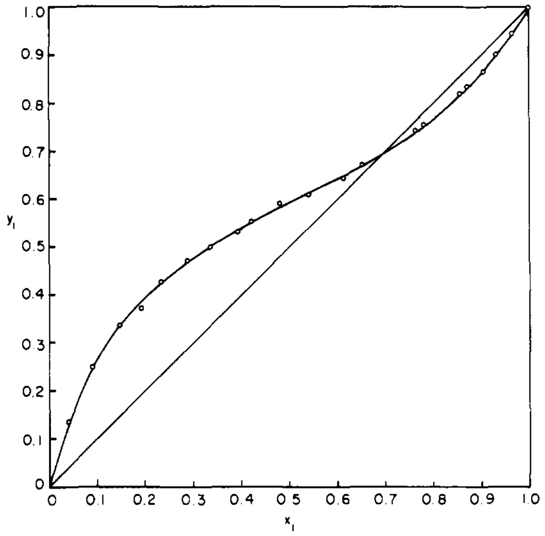

Figure 2. Equilibrium curve for the 1-butanol–chlorobenzene system: ○, experimental; —, theoretical.

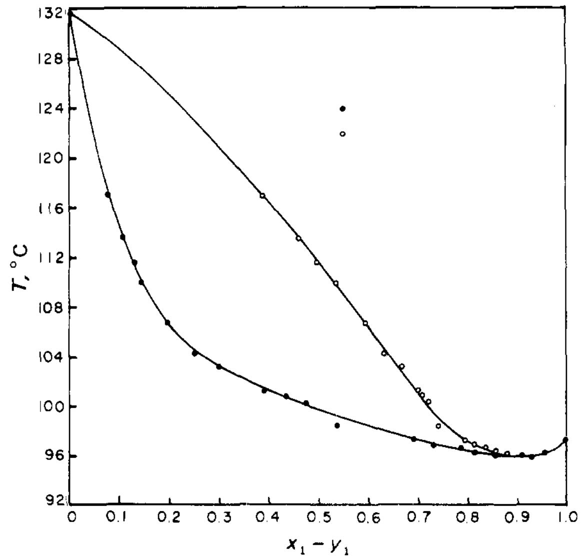

Figure 3. *T*–*x*–*y* diagram for the system 1-propanol–chlorobenzene: ●, bubble point (experimental); ○, dew point (experimental); —, theoretical.

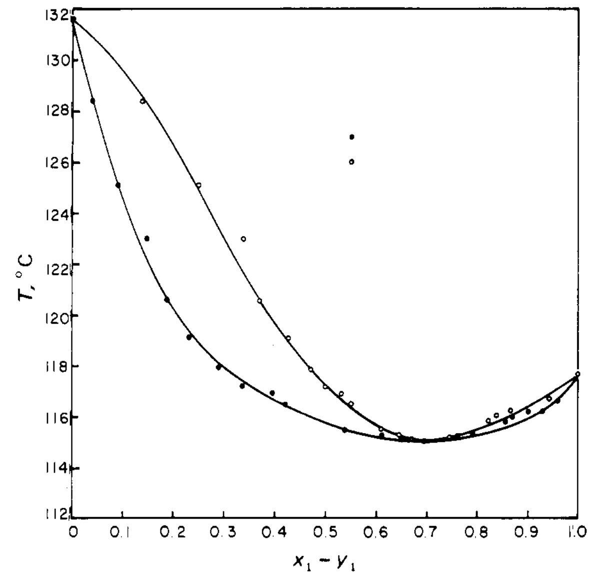

Figure 4. T-x-y diagram for the system 1-butanol–chlorobenzene: ●, bubble point (experimental); ○, dew point (experimental); —, theoretical.

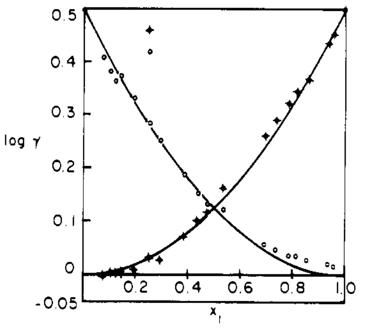

Figure 5. Activity coefficient vs. composition diagram for 1-propanol–chlorobenzene at 1 atm: ○, log γ_1 (experimental); ●, log γ_2 (experimental); —, theoretical.

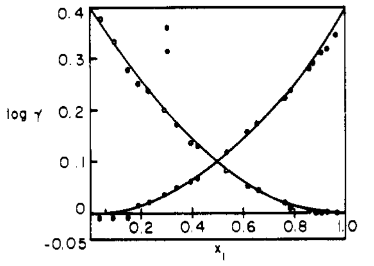

Figure 6. Activity coefficient vs. composition diagram for 1-butanol chlorobenzene at 1 atm: ○, log γ_1 (experimental); ●, log γ_2 (experimental); —, theoretical.

The vapor phase nonideality factor Z in the above equation is evaluated over the temperature range encountered for the systems using Wohl's generalized relation (*2*) applicable for the second virial coefficient of pure components in each system. The necessary vapor-pressure data for evaluating P^0 in the above equation are obtained from Wiessberger (*7*) and Hala et al. (*3*).

Discussion

The vapor-liquid equilibrium data for the systems 1-propanol + chlorobenzene and 1-butanol + chlorobenzene have not been reported so far in the literature. It is observed that both the systems show positive deviations from Raoult's law as seen from the values of activity coefficients which are greater than unity for each component in the two systems. Both the systems form minimum boiling azeotropes as is revealed by Figures 3 and 4.

Table IV. Azeotropic Data

	Azeotropic composition mole % (alcohol)		Bp, °C	
System	Exptl	Lit.	Exptl	Lit.
1-Propanol–chlorobenzene	91.0	88.2	96.0	96.5
1-Butanol–chlorobenzene	69.5	65.9	115.1	115.3

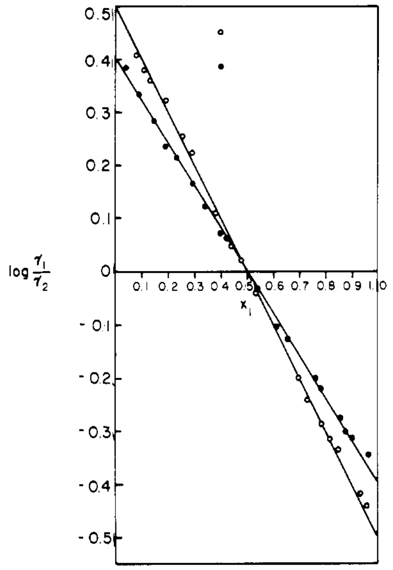

Figure 7. Redlich–Kister plot: ○, 1-propanol–chlorobenzene system; ●, 1-butanol–chlorobenzene system.

The experimental boiling points and azeotropic compositions are given in Table IV along with the literature values for comparison (*5*). In the 1-propanol + chlorobenzene system, it is difficult to obtain the experimental data for the solvent-rich region because of sharp changes in the boiling temperatures with change in the mole fraction of 1-propanol in this region. However, in order to get the limiting value of log γ_1 recourse is made to extrapolate the experimental data. For the above system, the results in and around the azeotropic point may be somewhat erroneous since changes in composition over that region are too small to be measured accurately with the refractometer used.

As per the classification of Ewell et al. (*1*), these systems belong to the combination of class II and V which should show positive deviations from Raoult's law and the present experimental results confirm the same.

The experimental data for both the systems are well correlated with Wohl's three-suffix Margule's equation (*8*). The constants A and B of the equation are obtained by curve fitting and trial and error procedures. As the constants A and B are equal in each system (for 1-propanol, $A = B = 0.5$; for 1-butanol, $A = B = 0.4$), the systems form symmetrical solutions. Hence the Van-Laar equation also fits the experimental data well.

Thermodynamic Consistency. Thermodynamic consistency of the experimental data for each system is tested by applying the Herington test (*4*). Net area of the plot from Figure 7 is found to be zero. Hence the data are thermodynamically consistent.

Glossary

P	total pressure in mmHg
P^0	vapor pressure of pure component in mmHg
x	liquid mole fraction
y	vapor mole fraction
Z	vapor phase nonideality factor

Greek:

γ	activity coefficient

Subscripts:

1	more volatile component

Literature Cited

(1) Ewell, R. H., Harrison, J. M., Berg, L., *Ind. Eng. Chem.*, **36**, 871 (1944).
(2) Hala, E., Pick, J., Fried, V., Vilim, O., "Vapour-Liquid Equilibrium", 2d English ed, Pergamon Press, London, 1967, p 123.
(3) Hala, E., Wichterle, I., Polak, J., Boublik, T., "Vapour-Liquid Equilibrium Data at Normal Pressures", Pergamon Press, London, 1968.
(4) Herington, E. F. G., *J. Inst. Pet. (London)*, **37**, 457 (1951).
(5) Horsely, L. H., "Azeotropic Data", American Chemical Society, Washington, D.C., 1952.
(6) Ward, S. H., Ph.D. Thesis, University of Texas, 1952.
(7) Wiessberger, A., Proskaners, E. D., Riddlick, T. A., Toops, E. E., "Organic Solvents", 2d ed, Interscience Publishers, London, 1955.
(8) Wohl, K., *Trans. Am. Inst. Chem. Eng.*, **42**, 215 (1946).

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Solubility in the System Sodium Orthophosphate, Acetone, and Water

Zvi Nirenberg, Beatrice Solenchyk, and Isaac Yaron*
Research & Development Authority, Ben-Gurion University, Beer-Sheva, Israel

Equilibrium in the ternary solid–liquid system of sodium orthophosphate, acetone, and water has been determined. Solubility isotherms for 10.0, 20.0, 31.5, and 40 °C are presented.

There has been considerable interest recently in processes of selective separation of inorganic salts from aqueous solutions through the addition of polar organic solvents. Very few data are available on the solid–liquid equilibrium of ternary and quaternary systems containing a polar organic component. Even less data are available for systems containing such a cheap and readily recoverable solvent as acetone. Thus, the well-known compilations of Linke and Seidel (*5*) and Stephen and Stephen (*6*), which comprise thousands of solubility tables, contain hardly a dozen or so such tables for systems including acetone. Emons et al. (*2*), Emons et al. (*3*), Emons et al. (*4*), Winkler and Emons (*7*), Cohen et al. (*1*), and others have determined equilibrium data for acetone-containing ternary and quaternary systems in relation to development of specific processes. In the course of our work on the selective separation of phosphorus compounds, we have investigated and present solid–liquid equilibrium data for the system sodium orthophosphate, acetone, and water at various temperatures.

Experimental Section

Materials. Analytical grade $Na_3PO_4\cdot 12H_2O$ from Merck and acetone from Frutarom were used. Purity of the reagents was rechecked. In all experiments doubly distilled water was used.

Procedure

Samples of acetone–water mixtures (50 ml) with varying acetone/water ratios were introduced into rubber-capped 100-ml flasks and thermostated in a Haake KT33 bath. Temperature was controlled within 0.1 °C. In experiments conducted at 31.5 °C small known amounts of sodium orthophosphate were progressively added to the acetone–water mixtures until saturation was reached, as indicated by the first appearance of a solid phase. When acetone/water ratios exceeded 2/3, $Na_3PO_4\cdot 12H_2O$ was added as a 9% aqueous solution in aliquots of 0.5 ml with a precision syringe. In other experiments, conducted at 10, 20, and 40 °C, excess $Na_3PO_4\cdot 12H_2O$ was always taken.

The saturated systems were equilibrated for 24 h and agitated periodically. Preliminary tests indicated that this duration was sufficient to reach equilibrium. Samples of the liquid phases (4.68 ml) were withdrawn with a calibrated syringe, and diluted immediately. They were analyzed for Na^+, P_2O_5, and acetone. Specific gravity of the liquid systems was determined. X-ray diffraction showed that the solid phase was $Na_3PO_4\cdot 12H_2O$ and remained unaltered.

Phosphorus was determined as P_2O_5 by the vanadomolybdate method, using a Bauch and Lomb Spectronic 200 UV spectrophotometer at 426 mμ. Accuracy of determination of P_2O_5 was ±0.25 ppm at concentrations of 50 ppm. Concentration of acetone was measured by iodometric titration with an accuracy of ±0.048 mg of acetone. Sodium was determined using a Pye Unicam SP90 atomic absorption spectrometer with an accuracy of ±2 ppm at 200 ppm full scale.

Results

Solubility data for sodium orthophosphate in acetone–water mixtures are summarized in Table I. Solubility isotherms at 10, 20, 31.5, and 40°C are presented in Figure 1. Compositions of the liquid phases in equilibrium with solid $Na_3PO_4\cdot 12H_2O$ are

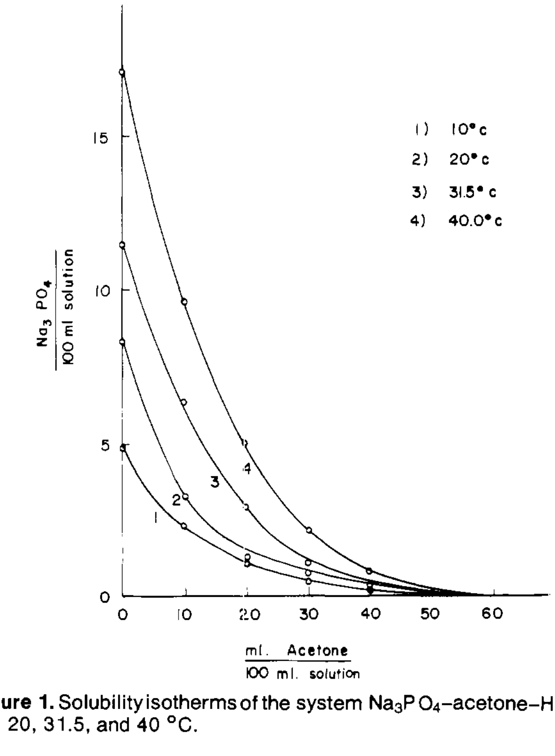

Figure 1. Solubility isotherms of the system Na_3PO_4–acetone–H_2O for 10, 20, 31.5, and 40 °C.