(18) Keyes, F.G., Project Squid, Massachusetts Institute of Technology, Cambridge, Tech. Rept. No. **37**, (April 1, 1952).
(19) Keyes, F.G., *Trans. ASME* **76**, 809 (1954).
(20) *Ibid.*, **77**, 1395 (1955).
(21) Landolt-Bornstein, Physikalisch-Chemische Tabellen.
(22) Lenoir, J.M., Comings, E.W., *Chem. Eng. Progr.* **47**, 223 (1951).
(23) Michels, A., Sengers, J.V., Van de Klundert, L.J.M., *Physica* **29**, 149 (1963).
(24) Mathur, S., Tondon, P.K., Saxena, S.C., *Mol. Phys.* **12**, 569 (1967).
(25) Rothman, A.J., Bromley, L.A., *Ind. Eng. Chem.* **47**, 899 (1955).
(26) Saxena, S.C., *Indian J. Phys.* **31**, 597 (1957).
(27) Saxena, S.C., Agrawal, J.P., *J. Chem. Phys.* **35**, 2107 (1961).
(28) Saxena, S.C., Gambhir, R.S., *Proc. Phys. Soc.* **81**, 788 (1963).
(29) Saxena, S.C., Gandhi, J.M., *Rajasthan Univ. Studies (Physics)* 1, 1 (1965).
(30) Saxena, S.C., Gandhi, J.M., *Rev. Mod. Phys.* **35**, 1022 (1963).
(31) Saksena, M.P., Saxena, S.C., *Phys. Fluids* **9**, 1595 (1966).
(32) Schäfer, K., Grundler, K.H., *Z. Elektrochem.* **63**, 449 (1959).
(33) Schäfer, K., Reiter, F.W., *Ibid.*, **61**, 1230 (1957).
(34) Sengers, J.V., Ph.D. dissertation, Amsterdam, 1962.
(35) Sengers, J.V., Bolk, W.T., Stigter, C.J., *Physica* **30**, 1018 (1964).
(36) Srivastava, B.N., Barua, A.K., *J. Chem. Phys.* **32**, 427 (1960).
(37) Srivastava, B.N., Saxena, S.C., *Proc. Phys. Soc. (London)* **B70**, 369, (1957).
(38) Touloukian, Y.S., Thermophysical Properties Research Center, Data Book, Vol. **2**, Chapter 1, Purdue University, Lafayette, Ind., 1966.
(39) Thomas, L.B., Golike, R.C., *J. Chem. Phys.* **22**, 300 (1954).
(40) Thornton, E., *Proc. Phys. Soc. (London)* **76**, 104 (1960); *Ibid.*, **77**, 1166 (1961).
(41) Thornton, E., Baker, W.A.D., *Proc. Phys. Soc. (London)* **80**, 1171 (1962).
(42) Vargaftik, N.B., Zimina, N.Kh., *High Temperature* **2**, 645 (1964).
(43) von Ubisch, H., *Arkiv Fysik* **16**, 93 (1959).
(44) Wachsmuth, *J. Phys. Z.* **9**, 235 (1908).
(45) Waelbroeck, F.G., Zuckerbrodt, P., *J. Chem. Phys.* **28**, 523 (1958).
(46) Walker, R.E., de Haas, N., Westenberg, A.A., *Phys. Fluids* **3**, 482 (1960).
(47) Weber, S., *Ann. Physik.* **54**, 48, 325 (1917).
(48) *Ibid.*, **82**, 479 (1927).
(49) Zaitseva, L.S., *J. Tech. Phys. USSR* **29**, 497 (1959).
(50) Zaitseva, L.S., *Soviet Phys. Tech. Phys.* **4**, 444 (1959).
(51) Liley, P.E., "The Thermal Conductivity of 46 Gases at Atmospheric Pressure," *Proc. Symp. Thermophys. Properties* **4th**, University of Maryland, April 1968.

RECEIVED for review December 30, 1966. Accepted February 23, 1968.

Linear Equilibrium Data for Ternary Liquid Systems and Binary Liquid-Gas Systems

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Published equilibrium data for 99 aqueous-organic systems, 47 organic-organic systems, and 39 liquid-gas systems have been tested for linearity. The best straight lines which pass either through the origin or through the mean values of the observations are considered. Slopes are tabulated for 28 systems having an error of less than 1% over the concentration range studied experimentally.

MUCH experimental work has been performed to determine equilibrium data for ternary liquid systems. Some systems are linear, some partially linear, and others nonlinear. Both mathematical expressions and graphical methods have been employed to represent the distribution data. Various laws of distribution have been proposed but these are frequently empirical and are not obeyed over wide concentration ranges (*8, 22*). The common assumption of a linear equilibrium relationship in many theoretical analyses of the performance of absorption and extraction equipment leads to simple expressions and avoids the cumbersome mathematics involved if nonlinear relationships are taken into account (*6, 10, 12, 13*). For the experimental verification of these theoretical analyses, and for most other experimental work on absorption or extraction equipment, it is clearly advantageous, if not essential, to employ systems exhibiting linear distribution relationships (*24, 25*). In preliminary design work, the use of linearized data enables quick answers to be obtained and can save valuable computer time for the more detailed calculations.

The purpose of compiling a set of systems with essentially linear equilibrium data is thus to enable the engineer either to select a system which he desires to be linear, or to confirm whether a particular system is linear, and to provide some estimate of the error in the assumption of linearity.

ANALYSIS OF DATA

Equilibrium data were obtained for a total of 185 systems, being made up of 99 aqueous-organic systems, 47 organic-organic systems, and 39 liquid-gas systems. These are arranged alphabetically according to the solute, and some are listed in Table I. Each separate set of data is termed a system and given a separate number, and so there are included in the list identical physical systems with data obtained by different authors or at different temperatures. The concentration units in which the data are given are also tabulated with reference to their source. The search was not exhaustive but limited to systems containing fairly common substances in which the solvents were reasonably immiscible.

As is usual in the literature, the solute concentrations

Table I. Systems with Error in Slope of Less than 1% over Concentration Range Studied Experimentally

System Number[a]	Solute	Organic Solvent		Temp., °C.	Concentration Units		Ref.
AO-10	Acetic acid	Methyl cyclohexanone		23	Weight %		(*17*)
AO-32	*n*-Butyric acid	Ethyl butyrate		28	Weight %		(*19*)
AO-38	*n*-Caproic acid	Methyl isobutyl ketone		20	G. moles/liter		(*3*)
AO-39	Diethylamine	Methyl isobutyl ketone		20	G. moles/liter		(*26*)
AO-40	Diethylamine	Toluene		20	G. moles/liter		(*26*)
AO-27	Formic acid	Methyl isobutyl ketone		25	G. moles/liter		(*3*)
AO-54	Lactic acid	1-Butanol		25	Weight %		(*18*)
AO-56	Malonic acid	Ethyl ether		25	Mg. moles/liter		(*23*)
AO-67	Nicotine	Benzene		25	G./liter		(*9*)
AO-68	Nicotine	Carbon tetrachloride		25	G./liter		(*9*)
AO-73	Oxalic acid	*n*-Amyl alcohol		Ambient	G./liter		(*1*)
AO-83	Propionic acid	Methyl butyrate		30	Weight %		(*15*)
AO-85	Propionic acid	Olive oil		25	G. moles/liter		(*4*)
AO-94	Succinic acid	*n*-Amyl alcohol		Ambient	G./liter		(*1*)
AO-96	Triethylamine	Methyl isobutyl ketone		20	G. moles/liter		(*26*)
AO-99	*n*-Valeric acid	Methyl isobutyl ketone		25	G. moles/liter		(*3*)
		Solvent x-Phase	Solvent y-Phase				
OO-24	Diphenylhexane	Decosane	Furfural	45	Weight %		(5)
	Solute Gas y-Phase	Liquid x-Phase		x-Phase	y-Phase		
LG-01	Ammonia	Water		0	Mm.Hg (partial)	G./g.	(*16*)
LG-02	Ammonia	Water		2	Mm.Hg (partial)	Cc./cc.[b]	
LG-13	Carbon dioxide	Water		20	Atm. (total)	Cc./cc.	(*20*)
LG-14	Carbon dioxide	Water		35	Atm. (total)	Cc./cc.	
LG-15	Carbon dioxide	Water		35	Atm. (total)	Cc./cc.	
LG-17	Carbon dioxide	Water		60	Atm. (total)	Cc./cc.	
LG-18	Carbon dioxide	Water		100	Atm. (total)	Cc./cc.	
LG-26	Propylene	Water		37.8	P.s.i.a. (total)	Mole %	(2)
LG-33	Dimethyl ether	Acetone		25	Mm.Hg (partial)	Mole fraction	(*11*)
LG-34	Dimethyl ether	Benzene		25	Mm.Hg (partial)	Mole fraction	(*11*)
LG-35	Dimethyl ether	Carbon tetrachloride		25	Mm.Hg (partial)	Mole fraction	(*11*)

[a] AO = aqueous-organic systems; OO = organic-organic systems; LG = liquid-gas systems. [b] Cc./cc. refers to cubic centimeters of gas (reduced to STP) dissolved in one cubic centimeter of liquid solvent.

x and y refer to the two conjugate phases (which separate out after a mixture of the solute and two solvents has been agitated until equilibrium is reached). For aqueous-organic systems the water phase is for the sake of uniformity always designated as the x-phase. For organic-organic systems the x- and y-phases are designated arbitrarily but are made explicit in Table I. The liquid phase is always taken as the x-phase in liquid-gas systems.

The best straight line through a number, n, of pairs of x, y values passes through the mean values $\bar{x}$, $\bar{y}$ and may be written

$$y - \bar{y} = b(x - \bar{x})$$

where b is the slope of the line. The best straight line through the origin of slope m may be written

$$y = mx$$

which corresponds to setting $\bar{x}$ and $\bar{y}$ equal to zero. For determining the best straight line through a set of points representing the distribution data, a functional relationship developed by Lindley (*14*) and summarized by Davies (*7*) was used. The assumption of equal variances was made on the basis that the experimental error in measuring the x-concentrations is usually of the same order as that of y-concentrations. This assumption is not critical, however, because as the ratio of the variances varies from zero to infinity, only slightly different lines are obtained which fall within the narrow limits set by the regression lines of y on x and x on y. Davies also gives expressions for the variances of the parameters describing the line.

For each system the best straight lines were obtained passing either through the mean values of the concentrations $\bar{x}$ and $\bar{y}$ or through the origin. Two concentration ranges were considered, one starting with the highest pair of concentrations and the other with the lowest. In each case, points were successively added until all the points were included. In this way, the lines having the minimum error in their slope could be found as well as the slope and error of the lines passing through all the points.

A typical equilibrium curve is shown in Figure 1 for the system AO-14 representing the distribution of acetic acid between water and methyl isobutyl ketone at 28° C. (*21*). The straight line through the origin illustrated has slope $m = 0.720$ with an error of 2.00% and applies up to an x concentration of 13.6 wt. %. The best straight line through the origin has slope $m = 0.617$ with error of 0.33% and applies up to an x concentration of 1.398 wt. %.

The best straight line in the concentration range x = 13.0 to 22.4 wt. %, as illustrated, passes through the mean values in this range $\bar{x} = 17.43$ and $\bar{y} = 14.13$ and has slope $b = 0.985$ with an error of 1.04%. For the full concentration range studied experimentally (x = 0.942 to 22.4 wt. %) the mean values are $\bar{x} = 10.786$ and $\bar{y} = 8.418$ and the slope $b = 0.859$ with an error of 2.07%. The straight line through the origin considering all the experimental points has slope $m = 0.804$ with an error of 1.71 wt. %. As both these errors in the over-all values of b and m are greater than 1%, system AO-14 is not included in Tables I and II.

Table II. Parameters of Systems with Error in Slope of Less than 1% over Concentration Range Studied Experimentally

Lower Concentration Region					Upper Concentration Region						
Upper concn. x-phase	Number of points, n	Slope, m	% error in m	System number	Lower concn. x-phase	Number of points, n	$\bar{x}$	$\bar{y}$	Error in $\bar{x}$ or $\bar{y}$	Slope, b	% error in b
31	5	0.979	0.33	AO-10	5.45	5	18.91	18.48	0.049	0.985	0.76
					15.15	4	22.28	21.83	0.029	0.973	0.58
6.5	6	6.635	0.73	AO-32	3.0	6	4.967	32.933	0.020	7.024	1.65
					4.7	4	5.700	38.075	0.006	6.588	0.92
0.01125	5	79.406	0.95	AO-38	0.00553	5	0.0084	0.6640	0.00002	85.467	1.05
0.1842	24	0.663	0.85	AO-39	0.00454	24	0.05350	0.03426	0.00016	0.688	0.57
					0.01068	21	0.06036	0.03880	0.00015	0.692	0.54
0.5899	20	0.557	0.61	AO-40	0.00099	20	00717	0.0383	0.0002	0.564	0.36
					0.00629	19	0.754	0.0403	0.0002	0.565	0.35
2.678	8	0.445	0.72	AO-47	0.170	8	0.9999	0.4393	0.0026	0.453	0.81
0.464	6	0.421	0.37								
12.5	8	0.928	0.75	AO-54	0.52	8	7.484	6.903	0.036	0.951	1.37
10.3	7	0.919	0.56		9.60	3	10.800	10.123	0.0004	1.045	0.05
94.6	6	0.148	0.59	AO-56	2.19	6	2.535	4.078	0.040	0.1487	0.86
3.8	2	0.135	0.19		22.30	3	50.440	7.537	0.018	0.1463	0.38
1.87	7	10.317	0.29	AO-67	0.45	7	1.126	11.586	0.002	10.446	0.56
1.65	6	10.276	0.23		0.61	6	1.238	12.748	0.002	10.499	0.48
1.97	10	9.551	0.73	AO-68	0.44	10	1.027	9.820	0.009	9.508	1.72
1.69	9	9.641	0.67								
81.6	22	0.362	1.09	AO-73	2.14	22	32.123	11.276	0.086	0.381	0.96
14.6	6	2.119	1.00	AO-83	6.2	6	10.750	22.850	0.095	2.025	3.74
11.8	4	2.159	0.63		11.8	3	13.200	27.867	0.013	1.536	1.34
0.218	5	0.166	0.38	AO-85	0.176	5	0.177	0.0179	0.0001	0.1662	0.75
67.5	12	0.607	0.96	AO-94	2.81	12	27.369	16.883	0.136	0.590	1.28
25.5	7	0.642	0.27								
0.02947	21	5.894	1.01	AO-96	0.00135	21	0.01447	0.08288	0.00005	6.305	0.53
					0.00519	18	0.01646	0.09515	0.00003	6.376	0.41
0.0358	4	25.143	0.94	AO-99	0.0198	4	0.0279	0.6988	0.0001	26.945	1.84
0.0255	2	24.568	0.79								
42.6	3	0.968	0.088	OO-24	10.0	3	25.700	24.967	0.193	0.953	2.10
24.5	2	0.987	0.28								
1.887	11	951.2	0.77	LG-01	0.997	11	1.476	1397	0.005	10.58	1.60
1.688	8	935.0	0.53		1.778	3	1.837	1788	0.001	1508	0.00
2483	11	0.722	0.77	LG-02	1312	11	1942	1397	3.87	0.803	1.60
2221	8	0.710	0.54								
26.87	7	1.844	2.98	LG-13	16.33	7	21.894	39.714	0.010	2.641	0.30
23.43	9	2.946	0.40	LG-14	9.98	9	16.851	49.778	0.031	2.834	0.75
13.38	3	2.996	0.15		20.39	3	22.033	64.333	0.004	2.633	0.37
29.6	11	2.614	0.23	LG-15	11.2	11	20.891	54.727	0.010	2.551	0.19
13.1	2	2.675	0.13								
26.6	17	4.60	0.98	LG-17	8.5	17	17.188	79.765	0.121	4.203	2.18
16.6	9	4.817	0.21		24.7	3	25.867	113.667	0.007	3.147	0.88
16.15	23	9.935	0.35	LG-18	6.35	23	11.127	110.130	0.027	10.277	0.84
15.91	22	0.908	0.32		6.84	21	11.576	115.000	0.023	10.241	0.77
0.09506	13	2415	0.98	LG-26	0.01122	23	0.0537	127.09	0.00040	2585	1.56
0.1893	7	6413	6.86	LG-33	0.0179	7	0.0978	670.03	0.0005	4456	0.81
					0.0378	6	0.1111	729.75	0.0000	4442	0.00
0.2100	7	4994	2.72	LG-34	0.023	7	0.1219	626.91	0.0000	4327	0.00
0.233	7	4828	3.20	LG-35	0.0300	7	0.1274	637.61	0.0000	4106	0.00
					0.1633	3	0.1985	929.33	0.0000	4168	0.00

RESULTS AND DISCUSSION

The available experimental data show that in 38% of the aqueous-organic systems, 26% of the organic-organic systems, and 77% of the liquid-gas systems investigated, there exists a linear region with an error in the slope of less than 1%. When the full concentration range studied experimentally is considered, the corresponding figures are 16, 2, and 31%. Of course, other linear regions may exist outside this concentration range.

Table I lists the 28 systems which have an error in the slope of less than 1% when the full concentration range studied experimentally is considered. Table II lists the parameters for these systems for lines both through the origin and through the mean values of the observations. For these systems, slopes are also given when there is a minimum error over a narrower concentration range. Systems LG-14 and LG-15 refer to data by the same author working with two different gas volumes. Table II shows that the difference in the slopes obtained from the two

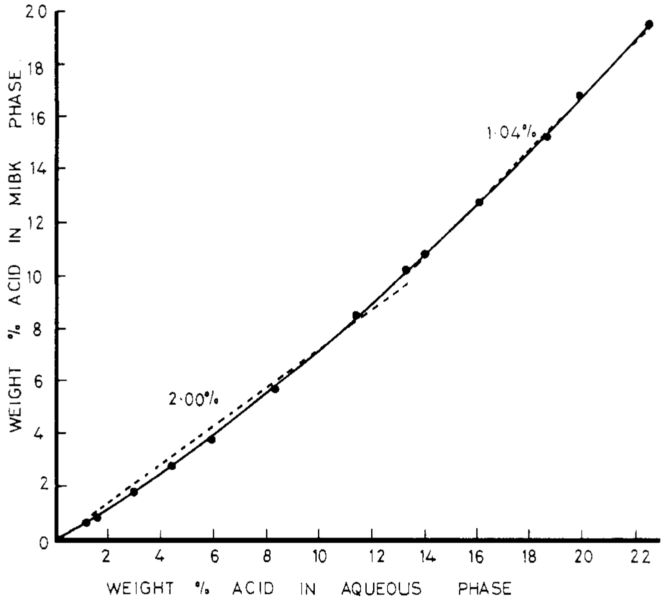

Figure 1. Distribution of acetic acid between water and methyl isobutyl ketone at 28 C. (system AO-14, reference 21)

experiments is greater than the individual error in either slope.

The use of linearized data is not suitable for every purpose. When careful design is required, it is best to fit curves of higher orders and to do the arithmetic on a computer. This is particularly true when one is interested in nonlinear portions of the equilibrium curve. An error of only 1% in the linearization of the data may lead to as much as say 10% error in the design. Finally, isothermal conditions of operation are implied, and this may not always be so, especially in the case of gas absorption.

NOMENCLATURE

b = slope of line passing through $\bar{x}, \bar{y}$
m = slope of line passing through origin
n = number of experimental points
x, y = concentrations
$\bar{x}$ = arithmetic mean of x values
$\bar{y}$ = arithmetic mean of y values

LITERATURE CITED

(1) Asselin, G.F., Comings, E.W., *Ind. Eng. Chem.* **42**, 1198 (1950).
(2) Azarnoosh, A., McKetta, J.J., J. CHEM. ENG. DATA **4**, 211 (1959).
(3) Bak, E., Geankoplis, C.J., CHEM. ENG. DATA SER. **3**, 256 (1958).
(4) Bodansky, M., Meigs, A.V., *J. Phys. Chem.* **36**, 814 (1936).
(5) Briggs, S.W., Comings, E.W., *Ind. Eng. Chem.* **35**, 411 (1943).
(6) Colburn, A.P., *Trans. Am. Inst. Chem. Engrs.* **35**, 211 (1939).
(7) Davies, O.L., "Statistical Methods in Research and Production," 3rd ed., pp. 173-4, Oliver and Boyd, Edinburgh, 1957.
(8) Elgin, J.C., and Browing, F.M., *Trans. Am. Inst. Chem. Engrs.* **31**, 639 (1935).
(9) Fowler, R.T., Noble, R.A.S., *J. Appl. Chem.* **4**, 546 (1954).
(10) Hartland, S., Mecklenburgh, J.C., *Chem. Eng. Sci.* **21**, 1209 (1966).
(11) Horiuti, J., Sci. Papers, *Inst. Phys. Chem. Res. (Tokyo)* **17**, 125 (1931).
(12) Klinkenberg, A., *Chem. Eng. Sci.* **1**, 86 (1951).
(13) Kremser, A., *Natl. Petrol. News.* **22**, 42 (1930).
(14) Lindley, D.V., *Suppl. J. Roy. Statist. Soc.* **9**, 218 (1947).
(15) Murty, N.S., Subrahmanyam, V., Murty, P.D., J. CHEM. ENG. DATA **11**, 335 (1966).
(16) Neuhausen, B.S., Patrick, W.A., *J. Phys. Chem.* **25**, 653 (1921).
(17) Othmer, D.F., White, R.E., Trueger, E., *Ind. Eng. Chem.* **33**, 1240 (1941).
(18) Petrits, V.E., Geankoplis, C.J., J. CHEM. ENG. DATA **4**, 197 (1959).
(19) Rao, M.R., Murty, P.D., J. CHEM. ENG. DATA **10**, 248 (1965).
(20) Sander, W., *Z. Physik. Chem.* **78**, 513 (1911).
(21) Scheibel, E.G., Karr, A.E., *Ind. Eng. Chem.* **42**, 1048 (1950).
(22) Sims, L.L., Bolme, D.W., J. CHEM. ENG. DATA **10**, 111 (1965).
(23) Smith, H.W., *J. Phys. Chem.* **25**, 160 (1921).
(24) Smoot, L.D., Babb, A.L., *Ind. Eng. Chem. Fundamentals* **1**, 93 (1962).
(25) Vermijs, V.J.A., Kramers, H., *Chem. Eng. Sci.* **3**, 56 (1954).
(26) Williams, K.C., Ellis, S.R.M., *J. Appl. Chem.* **11**, 492 (1961).

RECEIVED for review June 5, 1967. Accepted February 23, 1968.

Adsorption of Ferripolyphosphate

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A SUBSTANCE which possesses a surface of 100 to 1000 sq. meters per gram is considered a high-grade adsorber. The authors have prepared iron polyphosphate gels belonging to this class of absorbers. Their high capacity for basic materials, such as water and ammonia, and especially their low regeneration temperature should make them of interest where low heat with relatively high drying efficiency must be maintained.

EXPERIMENTAL PROCEDURES

Preparation. The preparation of these porous white gels has been reported (*4, 6*). They were obtained by the addition of solutions of sodium polyphosphate glass (30.5 grams of R-S unadjusted Calgon in 100 ml. of water), having the general formula $Na_{n+2}P_nO_{3n+1}$ and an average of nine phosphorus atoms per chain, to 0.5M iron (III) salt solutions. The gels were desiccated by washings with dioxane before drying in an oven. Analysis of the gels gave a molar Fe_2O_3–P_2O_5 ratio of 0.41. This ratio is equivalent to the

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