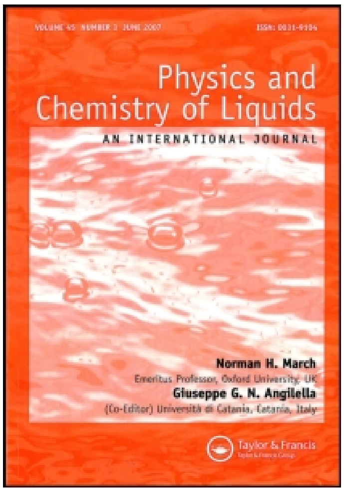
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Bubble-Point Data for the Systems: Bromobenzene(1)-Nitrobenzene(2) and Bromobenzene(1)-2-Nitrotoluene(2) at 200 and at 700 mm Hg

K. Dayananda Reddy[a]; M. V. Prabhakara Rao[a]; M. Ramakrishna[b]
[a] Chemical Laboratories, Sri Venkateswara University, Tirupati, A.P., India [b] Regional Research Laboratory, Hyderabad, India

To cite this Article Reddy, K. Dayananda , Rao, M. V. Prabhakara and Ramakrishna, M.(1985) 'Bubble-Point Data for the Systems: Bromobenzene(1)-Nitrobenzene(2) and Bromobenzene(1)-2-Nitrotoluene(2) at 200 and at 700 mm Hg', Physics and Chemistry of Liquids, 14: 3, 199 — 209

To link to this Article: DOI: 10.1080/00319108508080983

URL: http://dx.doi.org/10.1080/00319108508080983

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phys. Chem. Liq., 1985, Vol. 14, pp. 199-209
0031-9104/85/1403-0199$18.50/0

Printed in the United Kingdom

Bubble-Point Data for the Systems: Bromobenzene(1)-Nitrobenzene(2) and Bromobenzene(1)-2-Nitrotoluene(2) at 200 and at 700 mm Hg

K. DAYANANDA REDDY and M. V. PRABHAKARA RAO
Chemical Laboratories, Sri Venkateswara University Tirupati—517 502, (A.P.), India.

and

M. RAMAKRISHNA
Regional Research Laboratory, Hyderabad—500 009, India.

(*Received May 15, 1984*)

The bubble-point data were collected on a Swietoslawski type ebulliometer for the title systems each at 200 and 700 mm Hg. Calculated VLE data along with the activity coefficients and excess gibbs free energy values through the use of the Wilson equation are reported. The data are analysed for the nonideal behaviour of the systems. The pure-component Vapour–Pressure–temperature relationships are also presented.

1 INTRODUCTION

An accurate and complete knowledge of Vapour–liquid equilibrium is necessary for the design of distillation equipment. Generally Vapour–liquid equilibrium data are obtainable either at isothermal or at isobasic conditions. Most distillation processes are carried out at constant temperature, so that temperature–composition curves are more practical in making engineering calculations such as the number of plates, although for theoretical consideration the pressure–composition curves are preferable. As part of the continuing equilibrium study of halogen substituted aromatic hydrocarbon with nitrosubstituted aromatic hydrocarbons, Vapour–liquid equilibrium data on bromobenzene(1)-nitrobenzene(2) and bromobenzene(1)-2-nitrotoluene(2) systems each at 200 mm Hg as well as at 700 mm Hg were predicted because the data on these systems have not been reported in literature.

2 EXPERIMENTAL

Bromobenzene (BDH), nitrobenzene (BDH) and 2-nitrotoluene (Koch light Laboratories, England) were purified as per the methods described in Riddick and Bunger.[1] The purity of the samples was checked by measuring densities, refractive indices and boiling points. Densities were measured using a bicapillary pycnometer with an accuracy of 5 parts in 10^5. Refractive indices were determined using an Abbe's refractometer with an accuracy of ±0.0002. The boiling points of pure components and mixtures of known composition were measured on a Swietoslawski-type ebulliometer with an accuracy of ±0.2°C. The measured values are presented in Table I along with the literature values.[2,3]

The ebulliometer was connected to a vacuum system. The pressures were measured using mercury manometer with an accuracy of ±1 mm Hg. The temperatures were measured using a PT100 Thermometer which gave an

TABLE I

Densities, refractive indices and boiling points of the pure compounds at 303.15 k

	Density, ρ, g cm^{-3} at 303.15 K		Refractive indices at 293.15 K		Boiling point °K	
Compound	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Bromobenzene	1.48138	1.48148	1.5600	1.5604	429.2	429.2
Nitrobenzene	1.19325	1.79341	1.5525	1.5524	483.6	483.9
2-Nitrotoluene	1.1530	1.1531	1.5475*	1.5474*	493.4	493.5

* at 293.55 K

TABLE II

Antoine constants for the pure compounds with standard deviation

Compound	A	B	C	σ%
Bromobenzene	15.7468	3281.18	203.95	0.1
Nitrobenzene	16.3562	3992.91	200.271	0.39
2-nitrotoluene	13.8659	2382.41	109.19	0.86

accuracy of ±0.1°C. The detailed procedure was described previously.[4] Since the prediction of vapour–liquid equilibrium data involves the vapour pressure data of pure components, the same has been determined for bromobenzene, nitrobenzene, 2-nitrotoluene. The Antoine constants for the pure components obtained by the non-linear regression analysis[5] of the experimental data, are presented in Table II.

ISOBASIC BINARY SYSTEMS

The bubble or boiling points of the systems bromobenzene(1)-nitrobenzene(2) and bromobenzene(1)-2-nitrotoluene(2) were determined over the entire range of composition. Mixtures of different compositions were prepared by taking quantities (by weight) of the pure components. The boiling points for the known binary compositions were measured at 200 mm Hg and also at 700 mm Hg. The boiling point of a specified composition was first measured at 200 mm Hg. Then the pressure was raised to 700 mm Hg and the boiling point was determined. The system was brought back to 200 mm Hg when the boiling point measurement was repeated and finally the measurement was repeated at 700 mm Hg, thereby obtaining duplicate sets at both the pressures of interest. This procedure also helps us to detect any possible dissociation, and loss of material in the mixture under study.

3 RESULTS

The $t - x$ measurements were used for the data reduction Wilson equation[6, 7] was chosen to represent the composition and temperature dependence of liquid-phase activity coefficients γ_1 and γ_2.

$$\ln \gamma_1 = -\ln[x_1 + \Lambda_{12}x_2] + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \quad (1)$$

$$\ln \gamma_2 = -\ln[x_2 + \Lambda_{21}x_1] + x_1\left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right] \quad (2)$$

where

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp - \left[\frac{\lambda_{12} - \lambda_{11}}{RT}\right]$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L}\exp - \left[\frac{\lambda_{12} - \lambda_{22}}{RT}\right]$$

V_1^L and V_2^L are liquid molal volumes, $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ are temperature independent (to some extent) parameters, showing the energies of interaction between the molecules designated in the subscripts. The optimum-Wilson parameters $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ were obtained by minimising the objective function, ϕ,

$$\phi = \sum \left(\frac{P_{\text{cal}}}{P_{\text{exp}}} - 1.0 \right)^2 \tag{5}$$

using Nelder–Mead optimization technique,[5] are presented in Table III along with the standard deviation of the fit.

TABLE III

Wilson Parameters with standard deviation

System	$(\lambda_{12} - \lambda_{11})/R$	$(\lambda_{12} - \lambda_{22})/R$	Standard deviation °C
Bromobenzene(1)-nitrobenzene(2) at 200 mm Hg.	262.077	−219.991	0.28
Bromobenzene(1)-nitrobenzene(2) at 700 mm Hg.	−377.771	945.577	0.28
Bromobenzene(1)-2-nitrotoluene(2) at 200 mm Hg.	161.430	−280.852	0.21
Bromobenzene(1)-2-nitrotoluene(2) at 700 mm Hg.	−79.363	−54.522	0.20

4 DISCUSSION

The measured boiling points, calculated boiling points using Wilson equation and the ideal boiling points are presented in Table IV to VII. The vapour compositions were calculated using the following equation

$$y_1 = \frac{x_1 P_1^S \gamma_1}{P_{\text{cal}}} \tag{6}$$

The excess gibbs free energies were calculated using the activity coefficients

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{7}$$

The vapour–composition, activity coefficients and excess gibbs free energies are presented in Table VIII to XI. The vapour composition *vs.* mole fraction graphs and excess gibbs free energies G^E, *vs.* mole fraction graphs are represented in Figures 1 and 2. The G^E, values are negative over the entire

TABLE IV

Bromobenzene(1)-Nitrobenzene(2) $t - x$ at 200 mm Hg

x	t_{expt} °C	t_{cal} °C	t_{ideal} °C	$t_{expt} - t_{cal}$ °C
0.1527	147.5	147.8	146.9	−0.3
0.1527	147.6	147.8	146.9	−0.2
0.2435	141.7	141.1	140.4	0.3
0.2435	141.8	141.1	140.4	0.4
0.3233	136.7	136.5	135.5	0.2
0.3233	136.7	136.5	135.5	0.3
0.4176	131.0	131.3	130.4	−0.3
0.4176	131.2	131.3	130.4	−0.1
0.4308	130.5	130.6	129.8	−0.1
0.4308	130.5	130.6	129.8	−0.1
0.5318	125.7	125.9	125.2	−0.2
0.5318	125.8	125.9	125.2	−0.1
0.6532	121.2	120.9	120.5	0.3
0.6532	121.3	120.9	120.5	0.4
0.7731	116.5	116.7	116.5	−0.2
0.7731	116.5	116.7	116.5	−0.2
0.8216	115.0	115.1	115.0	−0.1
0.8213	115.0	115.1	115.0	−0.1
0.9033	112.2	112.7	112.6	−0.5
0.9003	112.3	112.7	112.6	−0.4

TABLE V

Bromobenzene(1)-Nitrobenzene(2) $t - x$ data at 700 mm Hg

x	t_{expt} °C	t_{cal} °C	t_{ideal} °C	$t_{expt} - t_{cal}$ °C
0.1527	191.5	191.9	193.6	−0.4
0.1527	191.6	191.9	193.6	−0.3
0.2435	185.0	184.7	187.0	0.3
0.2435	185.2	184.7	187.0	0.5
0.3233	179.2	179.1	181.8	0.1
0.3233	179.4	179.1	181.8	0.3
0.4176	173.0	174.4	176.4	−0.4
0.4176	172.9	174.4	176.4	−0.5
0.4308	172.5	172.7	175.7	−0.2
0.4308	172.5	172.7	175.7	−0.2
0.5318	167.6	167.4	170.6	0.2
0.5318	167.8	167.4	170.6	0.3
0.6532	162.2	162.2	165.1	0.0
0.6532	162.3	162.2	165.1	0.1
0.7731	158.0	158.1	160.4	−0.1
0.7731	158.1	158.1	160.4	0.0
0.8216	156.5	156.7	158.7	−0.2
0.8216	156.6	156.7	158.7	−0.1
0.9033	154.8	154.7	155.9	0.1
0.9033	154.9	154.7	155.9	0.2

TABLE VI

Bromobenzene(1)-2-nitrotoluene(2) $t - x$ data at 200 mm Hg

x	t_{expt} °C	t_{cal} °C	t_{ideal} °C	$t_{\text{expt}} - t_{\text{cal}}$ °C
0.1533	156.2	156.2	151.5	0.0
0.1533	156.4	156.2	151.5	0.2
0.3032	143.4	144.2	139.6	−0.8
0.3032	143.5	144.2	139.6	−0.7
0.3317	141.9	142.1	137.7	−0.2
0.3317	141.8	142.1	137.7	−0.3
0.4325	135.5	135.1	131.7	0.4
0.4325	135.4	135.1	131.7	0.3
0.5801	176.2	176.4	124.5	−0.2
0.5801	176.3	176.4	124.5	−0.1
0.6435	123.0	123.2	121.8	−0.2
0.6435	123.0	123.2	121.8	−0.2
0.6879	121.3	121.2	120.1	0.1
0.6879	121.3	121.2	120.1	0.1
0.7246	119.7	119.6	118.7	0.1
0.7246	119.8	119.6	118.7	0.2
0.8110	116.2	116.2	115.7	0.0
0.8110	116.3	116.2	115.7	0.1
0.9269	112.3	112.2	112.1	0.1
0.9269	112.4	112.2	112.1	0.2

TABLE VII

Bromobenzene(1)-2-nitrotoluene(1) $t - x$ data at 700 mm Hg

x	t_{expt} °C	t_{cal} °C	t_{ideal} °C	$t_{\text{expt}} - t_{\text{cal}}$ °C
0.1533	203.0	202.9	199.0	0.1
0.1533	203.2	202.9	199.0	0.3
0.3032	191.0	191.0	186.4	0.0
0.3032	190.8	191.0	186.4	−0.2
0.4325	181.7	181.8	177.8	−0.1
0.4325	181.6	181.8	177.8	−0.2
0.5969	170.6	171.4	168.8	−0.8
0.5969	170.8	171.4	168.8	−0.6
0.6435	168.8	168.8	166.6	0.0
0.6435	168.7	168.8	166.6	−0.1
0.6879	166.5	166.4	164.6	0.1
0.6879	166.6	166.4	164.6	0.2
0.7246	164.3	164.5	163.0	−0.2
0.7246	164.5	164.5	163.0	0.0
0.8110	160.6	160.4	159.5	0.2
0.8110	160.8	160.4	159.5	0.4
0.8800	158.3	157.4	156.9	0.9
0.8800	158.2	157.4	156.9	0.8

TABLE VIII

Vapour compositions, activity coefficients and excess gibbs free energies for the system Bromobenzene(1)-Nitrobenzene(2) at 200 mm Hg

x	y_{cal}	t_{cal}	γ_1	γ_2	G^E J mole^{-1}
0.05	0.1768	156.2	0.9272	0.9998	−14
0.10	0.3192	152.0	0.9334	0.9991	−26
0.15	0.4348	148.0	0.9397	0.9978	−38
0.20	0.5296	144.4	0.9460	0.9960	−48
0.25	0.6076	141.0	0.9522	0.9937	−56
0.30	0.6724	137.9	0.9582	0.9908	−63
0.35	0.7265	135.0	0.9640	0.9874	−69
0.40	0.7719	132.2	0.9694	0.9835	−73
0.45	0.8103	129.7	0.9744	0.9791	−75
0.50	0.8428	127.3	0.9789	0.9743	−76
0.55	0.8706	125.1	0.9831	0.9691	−75
0.60	0.8944	123.0	0.9868	0.9635	−72
0.65	0.9148	121.0	0.9900	0.9576	−68
0.70	0.9325	119.2	0.9927	0.9513	−63
0.75	0.9478	117.4	0.9950	0.9449	−57
0.80	0.9612	115.8	0.9969	0.9382	−47
0.85	0.9728	114.2	0.9983	0.9312	−38
0.90	0.9831	112.8	0.9992	0.9242	−27
0.95	0.9921	111.4	0.9998	0.9169	−14

TABLE IX

Vapour compositions, activity coefficients and excess gibbs free energies for the systems Bromobenzene(1)-Nitrobenzene(2) at 700 mm Hg

x	y_{cal}	t_{cal}	γ_1	γ_2	G^E J mole^{-1}
0.05	0.1680	201.5	1.1141	0.9999	20
0.10	0.3034	196.6	1.1118	0.9996	39
0.15	0.4141	192.1	1.1100	0.9991	55
0.20	0.5054	188.0	1.1087	0.9983	71
0.25	0.5815	184.2	1.1076	0.9974	86
0.30	0.6455	180.7	1.1066	0.9963	101
0.35	0.6995	177.4	1.1055	0.9951	115
0.40	0.7455	174.4	1.1042	0.9940	129
0.45	0.7849	171.6	1.1023	0.9933	143
0.50	0.8187	169.0	1.0998	0.9933	156
0.55	0.8478	166.6	1.0963	0.9945	169
0.60	0.8730	164.4	1.0916	0.9979	181
0.65	0.8948	162.3	1.0855	1.0050	192
0.70	0.9137	160.5	1.0776	1.0180	200
0.75	0.9302	158.8	1.0676	1.0409	204
0.80	0.9447	159.3	1.0554	1.0809	202
0.85	0.9575	156.0	1.0410	1.1521	190
0.90	0.9820	153.8	1.0089	1.5682	106
0.95	0.9820	153.8	1.0089	1.5682	106

TABLE X

Vapour compositions, activity coefficients and excess gibbs free energies for the system, Bromobenzene(1)-Nitrotoluene(2) at 200 mm Hg

x	y_{cal}	t_{cal} °C	γ_1	γ_2	G^E J mole^{-1}
0.05	0.1617	164.8	0.6862	0.9985	−71
0.10	0.3072	160.7	0.7206	0.9941	−132
0.15	0.4341	156.5	0.7532	0.9871	−184
0.20	0.5420	152.4	0.7838	0.9778	−227
0.25	0.6320	148.4	0.8125	0.9664	−262
0.30	0.7060	144.5	0.8391	0.9532	−288
0.35	0.7661	140.8	0.8636	0.9386	−306
0.40	0.8146	137.3	0.8859	0.9226	−318
0.45	0.8536	134.0	0.9060	0.9057	−328
0.50	0.8849	130.9	0.9240	0.8881	−320
0.55	0.9099	128.0	0.9399	0.8698	−311
0.60	0.9301	125.4	0.9536	0.8512	−296
0.65	0.9463	122.9	0.9654	0.8324	−276
0.70	0.9593	120.7	0.9753	0.8135	−250
0.75	0.9699	118.5	0.9833	0.7947	−220
0.80	0.9786	116.6	0.9896	0.7760	−184
0.85	0.9856	114.8	0.9943	0.7575	−144
0.90	0.9913	113.1	0.9975	0.7393	−100
0.95	0.9961	111.5	0.9994	0.7214	−52

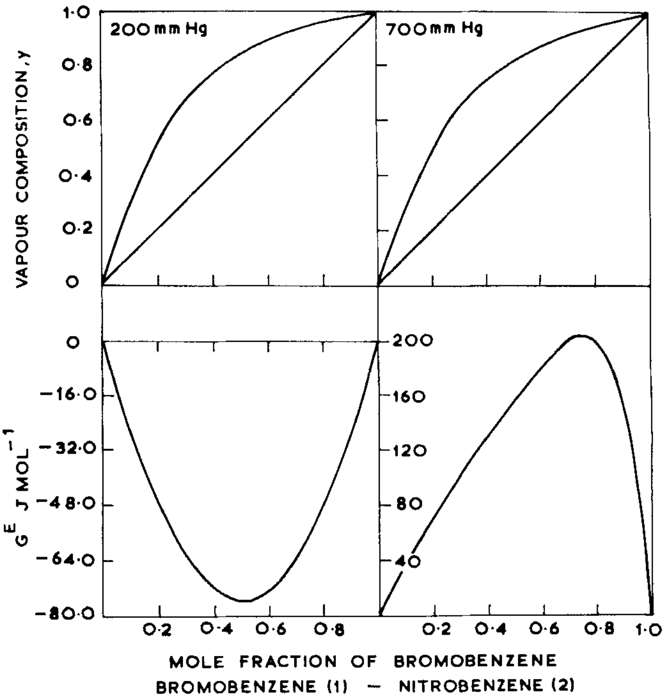


FIGURE 1 Vapour compositions and excess gibbs free energies for the system Bromobenzene(1)-Nitrobenzene(2) at 200 mm Hg and 700 mm Hg.

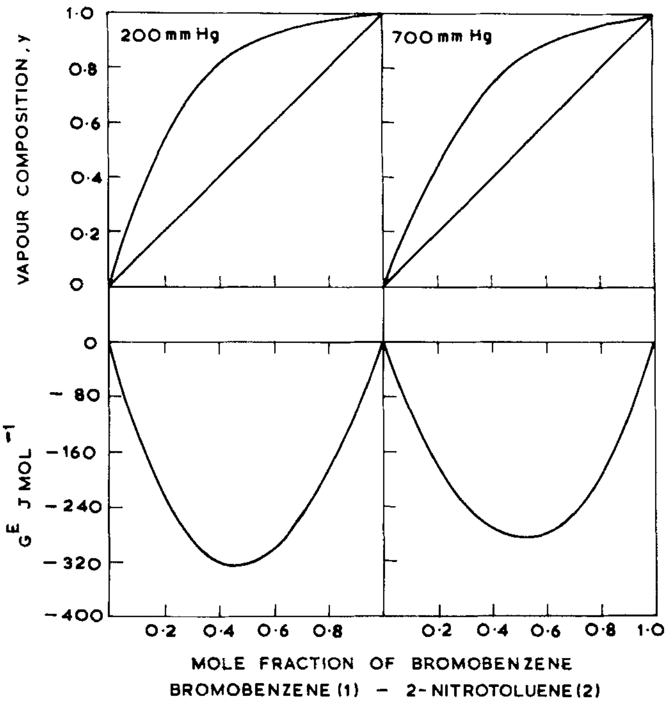


FIGURE 2 Vapour compositions and excess gibbs free energies for the system Bromobenzene(1)-2-Nitrotoluene(2) at 200 mm Hg and 700 mm Hg.

TABLE XI

Vapour composition activity coefficients and excess gibbs free energies for the system Bromobenzene(1)-2-nitrotoluene(2) at 700 mm Hg

x	y_{cal}	t_{cal} °C	γ_1	γ_2	G^E J mole^{-1}
0.05	0.1432	211.8	0.7771	0.9994	−51
0.10	0.2688	207.4	0.7935	0.9975	−98
0.15	0.3786	203.2	0.8099	0.9943	−139
0.20	0.4743	199.1	0.8262	0.9896	−176
0.25	0.5573	195.1	0.8424	0.9835	−207
0.30	0.6291	191.2	0.8583	0.9758	−234
0.35	0.6909	187.5	0.8740	0.9666	−255
0.40	0.7441	184.0	0.8893	0.9557	−271
0.45	0.7896	180.6	0.9041	0.9431	−282
0.50	0.8284	177.3	0.9184	0.9288	−287
0.55	0.8615	174.2	0.9319	0.9128	−286
0.60	0.8895	171.3	0.9446	0.8951	−279
0.65	0.9132	168.4	0.9564	0.8756	−267
0.70	0.9332	165.8	0.9670	0.8544	−248
0.75	0.9500	163.3	0.9765	0.8316	−223
0.80	0.9641	160.9	0.9845	0.8071	−192
0.85	0.9758	158.7	0.9911	0.7810	−154
0.90	0.9855	156.6	0.9959	0.7585	−110
0.95	0.9934	154.6	0.9990	0.7247	−58

range of composition, except in the binary system, bromobenzene(1)-nitrobenzene(2) at 700 mm Hg. G^E values are decreasing from nitrobenzene to 2-nitrotoluence. From the figures we can conclude that the systems are non-ideal.

Acknowledgement

One of the authors (KDR) is thankful to the Director and Head, Chemical Engineering Division, Regional Research Laboratory, Hyderabad, for providing the necessary facilities and to the CSIR, for awarding a Senior Research Fellowship.

References

1. J. A. Riddick, W. B. Bunger, *Techniques of Chemistry, Vol. 2 Organic Solvents*, Wiley-interscience, New York, 1970.
2. J. Timmermans, *Physicochemical Constants of Pure Organic Compounds*, Elsevier Publishing Company, Amsterdam, 1965.
3. J. A. Dean, ed., *Lange's Hand Book of Chemistry*. McGraw-Hill Company, New York, 1973.
4. E. Hala, J. Pick, O. Vilim, Fried, *Vapor–Liquid Equilibrium*, Pergamon Press, Oxford, 1967.
5. J. L. Kuester, J. H. Mize, *Optimization Techniques With Fortran*, McGraw-Hill Company, 1973.
6. G. M. Wilson, *J. Am. Chem. Soc.*, **86**, 127 (1964).
7. R. V. Orye, J. M. Prausnitz, *Ind. Engg. Chem.*, **57**, 18 (1965).

GLOSSARY

A, B, C	Antoine Constants
P	Pressure in mm Hg
t	temperature, °C
x	liquid phase mole fraction
y	vapour phase mole fraction

GREEK NOTATION

γ	Activity Coefficient
Λ	Wilson Parameter
$\lambda_{12} - \lambda_{11}$	interaction parameter in the Wilson equation, J mole^{-1}
$\lambda_{12} - \lambda_{22}$	interaction parameter in the Wilson equation, J mole^{-1}

SUBSCRIPTS

1. Bromobenzene
2. Nitrobenzene, 2-nitrotoluene