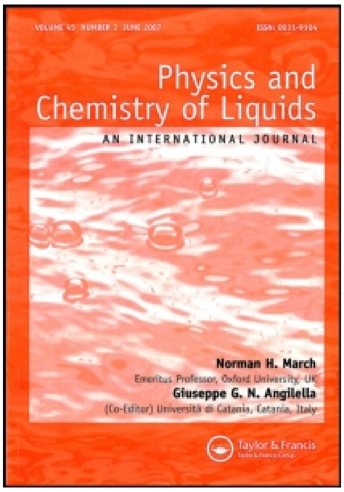

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Activity coefficients of binary mixtures of *m*-cresol selected compounds at 95.5 kPa

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To cite this Article Prasad, T. E. Vittal , Reddy, N. Malleshwara , Kiran, N. Anil and Prasad, D. H. L.(2006) 'Activity coefficients of binary mixtures of *m*-cresol selected compounds at 95.5 kPa', Physics and Chemistry of Liquids, 44: 3, 227 — 231

To link to this Article: DOI: 10.1080/00319100500329077

URL: http://dx.doi.org/10.1080/00319100500329077

Physics and Chemistry of Liquids
Vol. 44, No. 3, June 2006, 227–231

Taylor & Francis
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Activity coefficients of binary mixtures of *m*-cresol + selected compounds at 95.5 kPa

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(*Received 20 July 2005*)

Activity coefficients (at 95.5 kPa) over the entire composition range are obtained for the binary mixtures formed by *m*-cresol with: bromobenzene and *o*-, *m*- and *p*-xylenes. A Swietoslawski-type ebulliometer is used to measure the bubble point temperatures necessary to determine the activity coefficients. Wilson equation is used to represent the measured liquid phase composition *versus* temperature data and the computed values of the vapor phase composition and activity coefficients are tabulated.

Keywords: Activity coefficients; Bubble temperatures; *m*-Cresol; Bromobenzene; Xylenes

1. Introduction

This study on the activity coefficients of the binary mixtures formed by *m*-cresol with some selected compounds is in continuation of our recent systematic studies leading to the phase equilibria of the binary mixtures formed by different types of compounds [1,2]. There are no published vapor–liquid equilibrium data on the systems chosen for the present study.

2. Experimental section

2.1. *Method*

Bubble point temperatures of gravimetrically prepared liquid mixture samples (covering the whole composition range) are measured for all the four systems making use of

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Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online © 2006 Taylor & Francis
DOI: 10.1080/00319100500329077

a Swietoslawski-type ebulliometer similar to the one described by Hala *et al.* [3] and mentioned in some detail in our earlier paper [1]. The ebulliometer is connected to a vacuum pump and a dry nitrogen gas cylinder, with a closed-end manometer in line, to enable the measurement and maintenance of the total pressure of the system at 95.5 kPa, by adjusting the opening of the needle valve of the gas cylinder/the opening of the bypass line of the vacuum pump. The total pressure in this set of experiments is maintained within ±0.05 kPa of the chosen value, by frequently reading the mercury columns of the manometer and applying the needed corrective adjustment. A mercury-in-glass thermometer, calibrated by means of point-to-point comparison with a platinum resistance thermometer (certified by the National Institute of Standards and Technology, Boulder, USA), is used to measure the equilibrium temperature to an accuracy of ±0.05 K. The thermometer is placed in a thermowell (in the apparatus), the outer surface of which is constantly impinged by equilibrium vapor–liquid mixture. The thermowell has a small quantity of mercury to provide for good contact.

The mixtures to be studied are prepared gravimetrically, by weighing the required components making use of a Mettler balance accurate to 0.0001 g, and are stirred well before being introduced into the apparatus. The heating rate is maintained at a level capable of producing a condensate drop rate of 30 drops per min, following the suggestion of Hala *et al.* [3] by carefully adjusting the energy supply to the heater. The normally practiced method of subjecting the sample to the probable lowest pressure or highest temperature, likely to be encountered and reverting to ambient conditions several times, before starting the actual experiment is followed to achieve and retain the constancy of composition throughout the experiment. A gas chromatograph is used to verify the constancy of the composition of the sample at the beginning and at the end of each experimental phase equilibrium measurement. Equilibrium temperature is recorded, after the steady state conditions (observation of constant temperature and uniform boiling rate indicated by the maintenance of the chosen condensate liquid drop rate of 30 drops per min) are observed for at least 30 min.

2.2. *Materials*

Analytical reagent grade *m*-cresol (SISCO Research Laboratories, Mumbai, India) is stored over molecular sieves for two days and fractionally distilled twice.

Synthesis grade bromobenzene (E. Merck, Mumbai, India) is stored over silica gel for two days and fractionally distilled twice.

Ninety nine percent pure *o*-xylene (Lancaster, Lankshire, United Kingdom) is dried over silica gel and and fractionally distilled twice.

Analytical Reagent grade *m*-xylene and *p*-xylene (E. Merck, Mumbai, India) are fractionally distilled after drying over silica gel for two days.

The final step of the purification of all the liquids (fractional distillation) is carried by means of a packed column of height equivalent to 30 theoretical plates – only a few hours before the commencement of the phase equilibrium experiment and enough care is taken to prevent the absorption of moisture, oxidation, etc., during the intervening period. Based on the non-appearance of multiple significant peaks in the gas chromatograms and the comparison of the physical properties data with the literature values [4] presented in table 1, the pure liquids used in the present work are expected to be at least 99.9% pure.

Table 1. Comparison of the density (d) and refractive-index (n_D) with literature data [4].

Substance	T (K)	d (kg m^{-3}) This work	d (kg m^{-3}) Literature	n_D This work	n_D Literature
m-Cresol	298.15	1030.0	1030.19	1.5395	1.53960
Bromobenzene	293.15	1488.2	1488.20	1.5571	1.55709
o-Xylene	298.15	875.9	875.94	1.5030	1.50295
m-Xylene	298.15	860.1	860.09	1.4946	1.49464
p-Xylene	298.15	856.6	856.61	1.4933	1.49325

Table 2. Vapor–liquid equilibria of the binary mixtures of *m*-cresol with some selected compounds at 95.5 kPa.

x_1	T (K)	y_1	γ_1	γ_2	x_1	T (K)	y_1	γ_1	γ_2
	Bromobenzene(1) + *m*-cresol(2)					*o*-Xylene(1) + *m*-cresol(2)			
0.0000	473.75	0.0000	1.4706	1.0000	0.0000	473.75	0.0000	1.3483	1.0000
0.1030	463.65	0.3171	1.3145	1.0063	0.1115	459.35	0.4024	1.2677	1.0042
0.2056	456.45	0.4990	1.2083	1.0223	0.2200	449.15	0.6074	1.1988	1.0166
0.2717	452.75	0.5825	1.1579	1.0364	0.2921	444.15	0.6905	1.1611	1.0288
0.3411	449.35	0.6533	1.1168	1.0535	0.3637	439.75	0.7541	1.1274	1.0446
0.4021	446.75	0.7057	1.0884	1.0700	0.4155	436.95	0.7909	1.1059	1.0583
0.4631	444.95	0.7513	1.0658	1.0876	0.4646	434.55	0.8206	1.0877	1.0730
0.5502	440.95	0.8074	1.0415	1.1142	0.5552	430.55	0.8657	1.0591	1.1047
0.6396	437.85	0.8567	1.0240	1.1427	0.6342	427.35	0.8977	1.0392	1.1372
0.7105	435.55	0.8911	1.0143	1.1658	0.7055	424.75	0.9225	1.0250	1.1707
0.8055	432.45	0.9318	1.0058	1.1971	0.7781	422.35	0.9447	1.0140	1.2091
0.8650	430.85	0.9546	1.0026	1.2167	0.8421	420.25	0.9623	1.0070	1.2467
0.9255	429.15	0.9760	1.0008	1.2366	0.9120	418.05	0.9799	1.0022	1.2920
1.0000	420.05	1.0000	1.0000	1.2608	1.0000	415.45	1.0000	1.0000	1.3558
	m-Xylene(1) + *m*-cresol(2)					*p*-Xylene(1) + *m*-cresol(2)			
0.0000	473.75	0.0000	1.4146	1.0000	0.0000	473.75	0.0000	1.4450	1.0000
0.1105	456.45	0.4498	1.3438	1.0036	0.1103	456.25	0.4526	1.3361	1.0053
0.2200	444.75	0.6575	1.2755	1.0154	0.2200	444.75	0.6553	1.2445	1.0211
0.2902	438.85	0.7365	1.2341	1.0280	0.2755	440.15	0.7185	1.2051	1.0329
0.3609	431.55	0.7932	1.1948	1.0454	0.3309	436.45	0.7670	1.1701	1.0472
0.4060	428.95	0.8215	1.1712	1.0593	0.3907	432.85	0.8083	1.1370	1.0654
0.4586	425.15	0.8489	1.1452	1.0786	0.4586	429.25	0.8456	1.1048	1.0895
0.5406	421.75	0.8832	1.1082	1.1164	0.5403	425.45	0.8814	1.0729	1.1235
0.6298	418.55	0.9127	1.0732	1.1704	0.6291	421.75	0.9126	1.0458	1.1666
0.7205	414.95	0.9373	1.0437	1.2429	0.7304	417.95	0.9417	1.0233	1.2239
0.8360	413.75	0.9644	1.0161	1.3702	0.8357	414.35	0.9671	1.0084	1.2931
0.8765	412.85	0.9733	1.0094	1.4272	0.8655	413.45	0.9736	1.0055	1.3145
0.9108	410.25	0.9807	1.0050	1.4817	0.9088	412.05	0.9826	1.0025	1.3473
1.0000	473.55	1.0000	1.0000	1.6570	1.0000	409.25	1.0000	1.0000	1.4224

3. Results and discussion

The experimental composition (x_1) *versus* temperature (T) data, summarized in table 2, are fitted to the Wilson model, expressing the activity coefficients as

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

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

Table 3. Antoine constants used in $\ln(P/\mathrm{kPa}) = A - [B/(T/\mathrm{K}) + C]$.

Substance	A	B	C
m-Cresol	15.2496	4272.32	−74.09
Bromobenzene	13.7798	3312.98	−67.71
o-Xylene	14.0981	3395.57	−59.45
m-Xylene	14.1197	3366.99	−58.04
p-Xylene	14.0790	3346.65	−57.64

Table 4. Representation of the bubble point temperature measurements by Wilson model.

Mixture	$[(\lambda_{12} - \lambda_{11})/R]$ (K)	$[(\lambda_{12} - \lambda_{22})/R]$ (K)	SD (K)
Bromobenzene(1) + *m*-Cresol(2)	338.84	−134.93	0.04
o-Xylene(1) + *m*-Cresol(2)	119.54	225.76	0.03
m-Xylene(1) + *m*-Cresol(2)	−9.85	217.15	0.05
p-Xylene(1) + *m*-Cresol(2)	168.14	6.30	0.04

where

$$\Lambda_{12} = \frac{V_1^L}{V_2^L} \exp\left[-\left\{ \frac{\lambda_{12} - \lambda_{11}}{RT} \right\} \right] \tag{3}$$

and

$$\Lambda_{21} = \frac{V_2^L}{V_1^L} \exp\left[-\left\{ \frac{\lambda_{12} - \lambda_{22}}{RT} \right\} \right]. \tag{4}$$

The optimum Wilson parameters are obtained by minimizimg the objective function

$$\varphi = \left[\frac{P_{\mathrm{cal}}}{P_{\mathrm{expt}}} - 1 \right]^2. \tag{5}$$

The Nelder–Mead optimization technique, described by Kuster and Mize [5] is used. Vapor pressures, needed in the computations are calculated from the Antoine equation with the constants noted in table 3 for ready reference. These constants are found to represent the available pure liquid vapor pressure data (including the pure liquid boiling temperatures of the present experiments) with an average absolute deviation of 0.5%. Molar volumes of the pure liquids, calculated from the liquid density data given in table 1, are used as inputs to the calculation of the Wilson parameters. The results of the representation of the data by Wilson model are summarized in table 4. Vapor phase compositions determined from the Wilson model are also noted in table 2. In view of the care taken in carrying out the measurements and good representation by the model, the results presented in the article are expected to be useful for design purposes.

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