Journal of the Korean Chemical Society
2010, *Vol. 54, No. 1*
Printed in the Republic of Korea
DOI 10.5012/jkcs.2010.54.01.071

298.15 ~ 318.15 K 에서 2-브로모프로판-메탄올 이성분 혼합물의 밀도, 점성도, 여분 성질

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(접수 2009. 11. 11; 수정 2009. 12. 13; 게재확정 2009. 12. 22)

Densities, Viscosities and Excess Properties of 2-Bromopropane - Methanol Binary Mixtures at Temperature from (298.15 to 318.15) K

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(Received November 11, 2009; Revised December 13, 2009; Accepted December 22, 2009)

요약. 298.15~318.15 K 온도에서 디지탈 진동 U-tube densimeter 와 Ubbelohde 모세관 점성계을 사용하여 2-브로모프로판/메탄올 이성분 혼합물의 밀도와 점성도를 측정하였다. 온도와 농도에 대한 밀도와 점성도 상호 의존 관계를 조사하였다. 이성분 혼합물의 여분 몰부피와 여분 점성도를 실험으로 얻어진 밀도와 점성돌로부터 계산하여 구하였다. 모델이 실험치와 잘 부합됨을 발견하였다.

주제어: 밀도, 점성도, 여분 몰 부피, 여분 점성, 2-브로모프로판, 메탄올

ABSTRACT. The densities and viscosities of 2-bromopropane-methanol binary mixtures had been determined using an digital vibrating U-tube densimeter and Ubbelohde capillary viscometer respectively from (298.15 to 318.15) K. The dependence of densities and viscosities on temperature and concentration had been correlated. The excess molar volume and the excess viscosity of the binary system were calculated from the experimental density and viscosity data. The excess molar volumes were related to compositions by polynomial regression and regression parameters and total RMSD deviations were obtained; the excess viscosities was related to compositions by Redlich-Kister equation and regression coefficients and total RMSD deviation of the excess viscosity for 2-bromopropane and methanol binary system were obtained. The results showed that the model agreed very well with the experimental data.

Keywords: Densities, Viscosities, Excess molar volume, Excess viscosity, 2-Bromopropane, Methanol

INTRODUCTION

Isopropyl mercaptan is an important pharmaceutical intermediate and chemical material with wide use and optimum application prospect. Li *et al.*[1] have developed a new technique for the synthesis of isopropyl mercaptan using NaHS and 2-bromopropane as the raw material and methanol as the solvents.[1,2] This new technique is characterized by mild reaction conditions, high product purity and reduced waste. In the synthesis and purification process of isopropyl mercaptan, it is useful to know the basic data of densities and viscosities and so on of 2-bromopropane in methanol. The densities and viscosities are basic data used in chemical engineering designs, process optimization, and molecular thermodynamics study of solution. Therefore, in this study, densities and viscosities of 2-bromopropane in methanol had been measured at temperature from (298.15 to 318.15) K. From measurements of densities and viscosities, the excess molar volumes and the excess viscosities of 2-bromopropane in methanol were calculated. Results were fit to obtain the adjustable parameters and the deviations between the measured and fitted values. These quantities could be used to study the molecular interactions among the components of the mixture.

EXPERIMENTAL SECTION

Materials

2-bromopropane and methanol were of AR grade and they were obtained from Shanghai Chemical Reagent Co. and had mass fraction purities of 0.995. The water used in the experiments was deionized. The conductivity was less than 1×10^{-4} $S \cdot m^{-1}$.

Measurements of Densities

The densities of the mixtures and the corresponding pure substances were measured with an Anton Paar Model DMA 5000 digital vibrating U-tube densimeter, provided with automatic viscosity correction, having a stated accuracy of $\pm 5 \times 10^{-6}$

Table 1. Densities and Viscosities of 2-bromopropane and Methanol at 313.15 K

substance	ρ/g·cm^{-3}	ρ(lit)[5]/g·cm^{-3}	100 RD	η/mPa·s	η(lit)[6]/mPa·s	100 RD
methanol	0.7829	0.7835	-0.08	0.5045	0.5095	-0.99
2-bromopropane	1.2854	1.2843	0.09	0.4389	0.4330	1.34

g·cm^{-3}. The temperature in the cell was regulated to ± 0.001 K with a built-in solid-state thermo-stat. The temperature in the cell was measured by means of two integrated Pt 100 platinum thermometers, and the stability was better then ± 0.002 K. The reliability of the apparatus was verified daily with dry air and distilled freshly degassed water. To minimize the errors in composition, all mixtures were prepared by mass using the cell and the procedure described previously[3] and a Mettler AG 204 balance with a precision of 1×10^{-4} g. The uncertainty of the mole fraction calculation was less than $\pm 1 \times 10^{-4}$. All molar quantities were based on the IUPAC relative atomic mass table. The experimental uncertainty in density was about $\pm 1 \times 10^{-5}$ g·cm^{-3}.

Measurements of Viscosities

Viscosity was measured using a commercial Ubbelohde capillary viscometer (type 1836-A, Shanghai Glass Instruments Factory, China) of 0.55 mm diameter, calibrated with double-distilled water at (298.15 and 313.15) K. A thoroughly cleaned and perfectly dried viscometer, filled with experimental solutions, was placed exactly vertical in an insulated jacket, wherein constant temperature (± 0.02 K) was maintained by circulating water from a thermoelectric controller (type 501, Shanghai Laboratory Instrument Works Co., Ltd.) at the required temperature. After thermal stability was attained, the flow times of the solutions were recorded with an electronic digital stopwatch correct to ± 0.01 s. At least five repetitions of each datum point obtained were reproducible to ± 0.06 s, and the results were averaged. Because all flow times were greater than 200 s and the capillary diameter (0.55 mm) was far less than its length (100 mm), the kinetic energy and end corrections, respectively, were found to be negligible. The viscosity was then calculated from the relationship[4]

$$\frac{\eta}{\eta_w} = \frac{\rho t}{\rho_w t_w} \tag{1}$$

where η, ρ, t and η_w, ρ_w, t_w are the viscosity, density, and flow time of the mixture and water respectively come from the literature.[5] The uncertainty in the viscosity measurement is estimated to be ± 0.6%.

Experiment Reliability Proof

The measure densities and viscosities of 2-bromopropane and methanol at 313.15 K had been compared with literature values. The results were listed in *Table* 1. It could be seen that our experimental values of densities and viscosities were in good agreement with those reported in the literature.[6]

Table 2. Experimental Densities ρ/g·cm^{-3} of 2-bromopropane in Methanol as a Function of Mole Fraction from T = (298.15 to 313.15 K)

x	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0	0.7926	0.7913	0.7874	0.7829	0.7766
0.1	0.8551	0.8520	0.8466	0.8390	0.8286
0.2	0.9173	0.9093	0.8997	0.8901	0.8794
0.3	0.9743	0.9654	0.9540	0.9429	0.9313
0.4	1.0281	1.0195	1.0078	0.9957	0.9837
0.5	1.0806	1.0719	1.0599	1.0471	1.0342
0.6	1.1308	1.1215	1.1085	1.0974	1.0831
0.7	1.1801	1.1693	1.1571	1.1458	1.1326
0.8	1.2242	1.2157	1.2035	1.1932	1.1805
0.9	1.2678	1.2600	1.2486	1.2382	1.2265

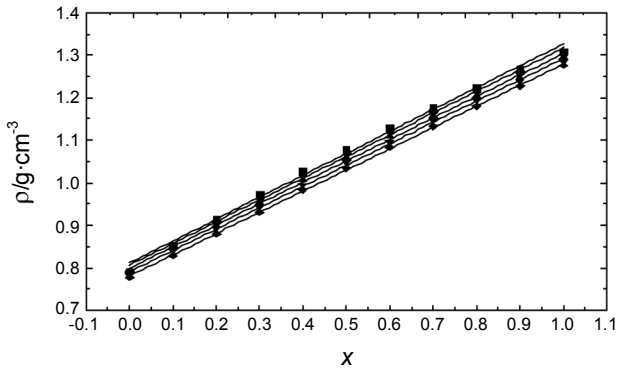

Fig. 1. Density of 2-bromopropane in methanol at various temperatures. ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; ◆, 318.15 K; —, calculated.

RESULTS AND DISCUSSION

The experimental densities at various temperatures as a function of mole fraction for 2-bromopropane in methanol were presented in *Table* 2, *Fig*. 1 and *Fig*. 2. It could be seen from *Table* 2 and *Fig*. 1 that densities decreased with increasing temperature at a definite concentration of 2-bromopropane in methanol and increased with increasing concentration of 2-bromopropane in methanol at constant temperature. From *Fig*. 2, it could be found that densities and temperature gave the straight linear relationship.

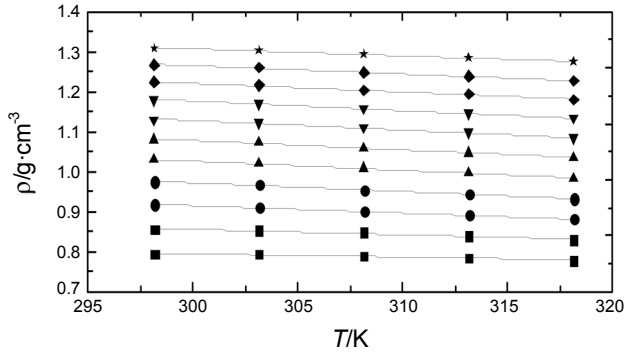

Fig. 2. Relative changes in density of 2-bromopropane in methanol on temperature at different mole fraction. ■, 0.0; □, 0.1; ●, 0.2; ○, 0.3; ▲, 0.4; △, 0.5; ▼, 0.6; ▽, 0.7; ◆, 0.8; ◇, 0.9; ★, 1.0.

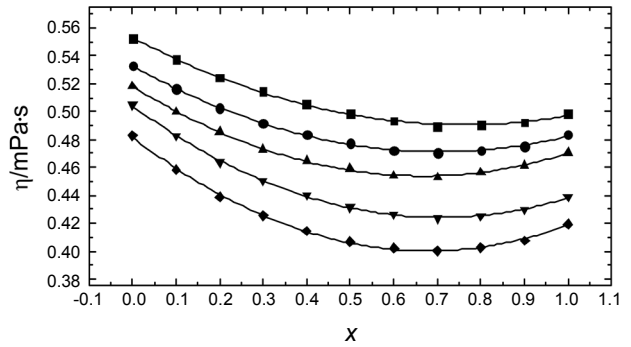

Fig. 3. Viscosity of 2-bromopropane in methanol at various temperatures. ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; ◆, 318.15 K; —, calculated.

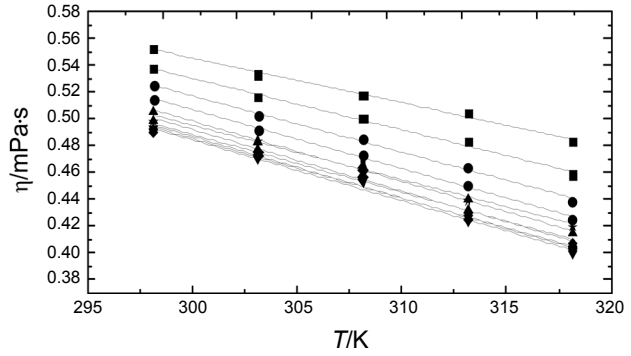

Fig. 4. Relative changes in viscosity of 2-bromopropane in methanol on temperature at different mole fraction. ■, 0.0; □, 0.1; ●, 0.2; ○, 0.3; ▲, 0.4; △, 0.5; ▼, 0.6; ▽, 0.7; ◆, 0.8; ◇, 0.9; ★, 1.0.

The experimental viscosities at various temperatures as a function of mole fraction for 2-bromopropane in methanol were presented in *Table* 3 and *Fig*. 3 and *Fig*. 4. It could be found from *Table* 3 and *Fig*. 3 that viscosities decreased with increasing temperature at a definite concentration of 2-bromopropane in methanol, and decreased with increasing concentration of 2-bromopropane in methanol at constant temperature, reached a minimum value at about x = ~ 0.6 and then increased. The temperature influenced strongly the viscosity but the compositions for the minimum in viscosity were found to be almost constant and independent of temperature. From *Fig*. 4 it could be found that viscosities and temperature gave the straight linear relationship.

Table 3. Experimental Viscosities η/mPa·s of 2-Bromopropane in Methanol as a Function of Mole Fraction from T = (298.15 to 313.15 K)

x	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0	0.5523	0.5327	0.5179	0.5045	0.4829
0.1	0.5372	0.5161	0.5000	0.4824	0.4583
0.2	0.5242	0.5023	0.4852	0.4639	0.4389
0.3	0.5144	0.4919	0.4729	0.4502	0.4256
0.4	0.5051	0.4833	0.4650	0.4400	0.4144
0.5	0.4984	0.4774	0.4589	0.4318	0.4069
0.6	0.4931	0.4722	0.4540	0.4263	0.4019
0.7	0.4897	0.4702	0.4529	0.4236	0.4002
0.8	0.4900	0.4718	0.4562	0.4250	0.4027
0.9	0.4922	0.4752	0.4612	0.4299	0.4075

Correlation of Density

The dependence of density on temperature and concentration were calculated from the equation 2.[7]

$$\rho = A_0 + A_1 x \qquad A_0 = a_0 + a_1 T, \qquad A_1 = a_2 + a_3 T \tag{2}$$

where, x represents mole fraction of 2-bromopropane, ρ is the density of the mixtures, T is the absolute temperature; and a_0 - a_5 are regression coefficients. The calculated values and deviations were listed in *Table* 4. Densities were calculated according to eq 2 using values for parameters a_0 - a_5 that were listed in *Table* 5. Some calculated results could be seen in *Fig*. 1.

The root-mean-square deviation is defined by.[8]

$$\mathrm{RMSD} = \left[\frac{1}{N-1} \sum_{i=1}^{N} (\rho_{ci} - \rho_i)^2 \right]^{1/2} \tag{3}$$

Where N is the number of experimental points, ρ_{ci} represents the densities calculated from equations, and ρ_i represents the experimental density values.

The relative average deviations (RAD) is defined as,[8]

$$\mathrm{RAD} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{\rho_i - \rho_{ci}}{\rho_i} \right| \tag{4}$$

From comparison of the calculated and experimental values, the total RMSD and average relative deviations (RAD) of 55 data points were less than 2% and 0.1%, respectively. It was clear that eq 2 could be successfully used to correlate densities

Table 4. Regression coefficient and deviation of densities and viscosities for the methanol-2-bromopropane binary system

T/K	A_0	A_1	10^3 RAD	10^2 RMSD	B_0	B_1	B_2	10^3 RAD	10^3 RMSD
295.15	0.8111	0.516	9.09	1.76	0.553	-0.164	0.108	1.26	1.23
300.15	0.806	0.511	7.12	1.41	0.533	-0.175	0.125	1.35	1.23
305.15	0.799	0.505	5.31	1.07	0.518	-0.193	0.145	1.16	1.09
310.15	0.790	0.502	3.81	0.759	0.504	-0.226	0.161	1.44	1.15
315.15	0.781	0.499	2.62	0.491	0.482	-0240	0.177	1.89	1.62

Table 5. Regression coefficients of densities and viscosities for the methanol--2-bromopropane binary system

a_0	a_1	a_2	a_3	b_0	b_1	b_2	b_3	b_4	b_5
1.27	-0.00154	0.761	-0.000835	1.56	-0.00343	1.04	-0.00406	-0.916	0.00347

Table 6. Excess Molar Volumes of 2-Bromopropane-methanol

x	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	1.1708	1.2678	1.3383	1.5522	1.8533
0.2	1.7183	2.1342	2.4878	2.8262	3.1403
0.3	2.1163	2.5674	3.0109	3.4394	3.7948
0.4	2.3079	2.6975	3.1146	3.5908	3.9440
0.5	2.2157	2.5770	2.9711	3.4624	3.8549
0.6	1.9658	2.3375	2.7594	3.0928	3.5596
0.7	1.5014	1.9412	2.2566	2.5713	2.9133
0.8	1.1632	1.3932	1.6675	1.8694	2.1437
0.9	0.6297	0.7696	0.9412	1.1217	1.2837
1.0	0.0000	0.0000	0.0000	0.0000	0.0000

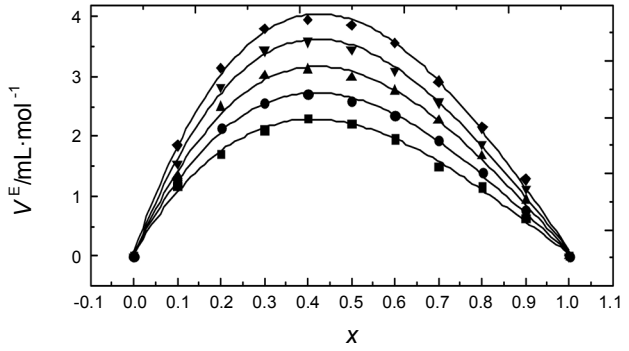

Fig. 5. Excess molar volume for 2-bromopropane and methanol for whole range of mole fractions at different temperatures. ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; ◆, 318.15 K; —, calculated.

of methanol-2-bromopropane binary mixtures.

Excess Molar Volumes and Excess Viscosities

The excess molar volumes V^E and the excess viscosities were calculated from the equation 6, 7, respectively.[7]

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho_{12}} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \quad (6)$$

where, x_1 and x_2 represent mole fraction of 2-bromopropane and methanol, respectively, and M_1 and M_2 represent molar masses of 2-bromopropane and methanol, respectively, ρ_{12}, ρ_1 and ρ_2 are the densities of the mixtures, or 2-bromopropane and methanol, respectively.

$$\Delta\eta = \eta_{12} - (x_1\eta_1 + x_2\eta_2) \quad (7)$$

where, η_{12} is the viscosity of the mixture; η_1 and η_2 is the viscosity of 2-bromopropane and methanol, respectively.

The excess molar volume (V^E) calculated from the density data was listed in *Table* 6. The excess molar volume over the entire range of mole fraction *x* and temperature range between (298.15 and 318.15) K were plotted in *Fig*. 5. It could be seen that the values of the excess molar volume (V^E) were found to be positive and a great temperature effect for the whole concentration was found. The excess molar volume maximum was found to be almost temperature independent at x = ~ 0.4. The excess molar volume represented the difference in molar specific value for 2-bromopropane and methanol, if the value was large, it indicated that there was a volume contraction in the system and also indicated that 2-bromopropane and methanol were completely miscible system.

The excess viscosities calculated from the viscosity data was listed in *Table* 7. The excess viscosities over the entire range of mole fraction x and temperature range between (298.15 and 318.15) K were plotted in *Fig*. 6. It could be seen that the values of the excess viscosities were found to be negative, and the excess viscosities decreased with increasing concentration, reached a minimum value at about x = ~ 0.5 and then increased. Increasing temperature decreased the value of the excess viscosities at a definite concentration 2-bromopropane in methanol of for 2-bromopropane and methanol binary system, but the composition for the minimum value was almost constant.

The excess molar volume (V^E) was correlated by the equation 8,[7]

$$V^E = A_0^{'} + A_1^{'}x + A_2^{'}x^2 + A_3^{'}x^3 \quad (8)$$

where, $A_0^{'}$, $A_1^{'}$, A_2 and $A_3^{'}$ are equation parameters; x is mole fraction of 2-bromopropane.

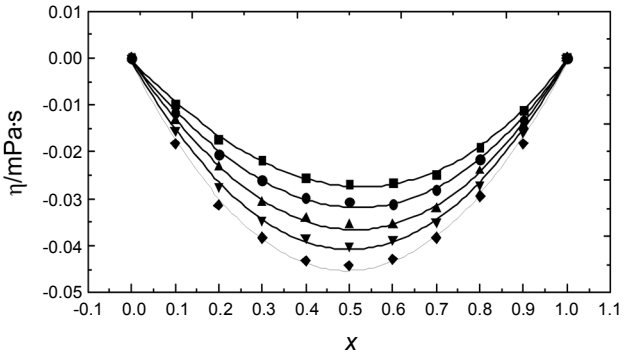

Fig. 6. Excess viscosity for 2-bromopropane and methanol for whole range of mole fractions at different temperatures. ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; ◆, 318.15 K; —, calculated.

Table 7. Excess Viscosities of 2-Bromopropane - methanol

x	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	-0.0097	-0.0117	-0.0132	-0.0155	-0.0182
0.2	-0.0172	-0.0206	-0.0233	-0.0275	-0.0313
0.3	-0.0217	-0.0261	-0.0309	-0.0346	-0.0383
0.4	-0.0255	-0.0297	-0.0341	-0.0382	-0.0432
0.5	-0.0268	-0.0307	-0.0355	-0.0399	-0.0442
0.6	-0.0267	-0.0310	-0.0357	-0.0388	-0.0429
0.7	-0.0247	-0.0281	-0.0320	-0.0349	-0.0383
0.8	-0.0189	-0.0215	-0.0241	-0.0270	-0.0294
0.9	-0.0113	-0.0132	-0.0144	-0.0156	-0.0183
1.0	0.0000	0.0000	0.0000	0.0000	0.0000

The excess properties indicate the departure from the ideal condition and can be correlated by the Redlich-Kister equation,[7]

$$\Delta\eta = x_1 x_2 \sum_{i=1}^{n} B_i^{'}(x_1 - x_2)^i \quad (9)$$

where, x_1 and x_2 is mole fraction of 2-bromopropane and solvent. $B_i^{'}$ is the optimum values for the Redlich-Kister coefficients.

The optimum values for polynomial regression coefficients ($A_i^{'}$) and the Redlich-Kister coefficients ($B_i^{'}$) were obtained respectively by fitting experimental data at various temperature and concentration, the regression coefficients of the excess volume and the excess viscosity along with their deviation were listed in *Table* 8 and *Table* 9, respectively. Some results could be seen in *Fig*. 5 and *Fig*. 6. From comparison of the calculated and experimental values of the excess volume and the excess viscosity, the total RMSD of 55 data points were less than 9% and 0.1%, respectively, and average relative deviations (RAD) were less than 2.88% and 2.39%, respectively. On the basis of the obtained RAD and RMSD values, we concluded that eq 8 and eq 9 could be successfully used for the correlation of the excess volume and the excess viscosity.

CONCLUSION

Densities and viscosities of 2-bromopropane and methanol were measured for the entire range of molar fractions and for the temperature range between (298.15 and 318.15) K. and the Densities and viscosities on temperature and concentration were calculated by the regression. Regression coefficients and deviation were obtained.

The excess molar volume and the excess viscosity were determined from the experimental density and viscosity data. The

Table 8. Regression coefficients and deviation of the excess volume for 2-bromopropane and methanol binary system

T/K	$A_0^{'}$	$A_1^{'}$	$A_2^{'}$	$A_3^{'}$	Correlation coefficient	100 RAD	100 RMSD
298.15	0.0487	12	-18.69	6.68	0.9941	2.88	5.41
303.15	0.0382	14.2	-21.71	7.52	0.997	1.94	4.55
308.15	0.00810	16.41	-24.65	8.3	0.9942	2.79	7.41
313.15	0.00640	18.93	-28.66	9.82	0.9952	2.71	7.75
318.15	0.0669	20.47	-30.34	9.91	0.9951	2.34	8.60

Table 9. Regression coefficients and deviation of the excess viscosity for 2-bromopropane and methanol binary system

T/K	$B_0^{'}$	$B_1^{'}$	$B_2^{'}$	$B_3^{'}$	Correlation coefficient	100 RAD	10^3 RMSD
298.15	-0.000462	-0.0950	0.0696	0.0255	0.9971	-1.76	0.451
303.15	-0.000607	-0.116	0.0975	0.0183	0.9958	-1.95	0.632
308.15	-0.000412	-0.138	0.123	0.0143	0.9973	-1.62	0.588
313.15	-0.000680	-0.160	0.159	0.000952	0.9966	-1.86	0.727
318.15	-0.00106	-0.182	0.190	-0.00890	0.9947	-2.39	1.00

excess molar volumes were related to compositions by polynomial regression and regression parameters and total RMSD deviations were obtained; the excess viscosities was related to compositions by Redlich-Kister equation and regression coefficients and total RMSD deviation of the excess viscosity for 2-bromopropane and methanol binary system were obtained. The total RMSD deviations of two equations were less than 8.6% and 0.1%, respectively. The results showed that the model agreed very well with the experimental data.

REFERENCES

1. Li, H.; Zhang, Z.; Zhao, L.; Guo, F. *Chem. Reagents*. **2008**, *30*, 826.
2. Liu, Y. P; Sun, B. G.; Xie, J. C.; Zheng, F. P.; Xiao, Y. *Chem. Reagents*. **2004**, *26*, 291.
3. Tasic, A. Ž.; Grozdanic, D. K.; Djordjevic, B. D.; Šerbanovic, S. P.; Radojkovic, N. *J. Chem. Eng. Data*. **1995**, *40*, 586.
4. Wang, J. Y.; Wang, F. A.; Zhang, P. *J. Chem. Eng. Data*. **2008**, *53*, 648.
5. Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed,; McGraw-Hill: New York, 1999.
6. Reid, E. E.; M. A.; Ph.D.; L L. D. *Organic Chemistry of Bivalent Sulfur*; Chemistry Publishing Co., INC.,: New York, 1963. Vol. V, p 19.
7. Song, X. F.; Luo, Y.; Wang, J.; Yu, J. G. *J. of East China Univ. of Sci. and Tech. (Natural Science)*. **2007**, *33*, 750.
8. Li, H.; Guo, F.; Hu, G. Q. *J. Chem. Eng. Data*. **2009**, *54*, 2100.