DENSITY AND VISCOSITY CALCULATIONS FOR POLAR SOLUTIONS VIA NEURAL NETWORKS

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Density and viscosity were measured for solutions of butylamine + ethanol, butylamine + ethanol + water, and butylamine + benzylamine + water over a temperature range of 303.15 - 323.15 K at atmospheric pressure. Three artificial neural networks were also developed for predicting the density and viscosity of multicomponent polar liquid mixtures with emphasis on aqueous solutions. The connection weights of the networks were determined from binary data. Those trained networks were capable of calculating density to within $\pm 1\%$ for both binary and ternary systems and calculating viscosity generally as good as that from the corresponding-states model of Lee and Wei for aqueous systems.

Introduction

The composition effects on viscosity are usually significant and asymmetric in aqueous solutions. This behavior could result from aggregate formation between water and solute molecules⁴⁾. As noted in the literature^{9, 14)}, most viscosity models which are applicable to non-aqueous mixtures may no longer be applied to aqueous solutions. Wei and Rowley¹⁹⁾ proposed a local-composition model to account for non-random mixing in highly polar solutions. This model predicted the kinematic viscosity of non-aqueous solutions quite well. However, no aqueous solutions were tested in the study. The same can be said for most group-contribution models^{1, 20)}. A useful modification was made by Papaloannou *et al.*¹³⁾ who incorporated a van Laar-type mixing rule into the Teja-Rice model¹⁶⁾. Recently, Lee and Wei⁹⁾ developed a corresponding-states viscosity model by utilizing oxygen, octane, and water as reference fluids. The model with a quadratic mixing rule yielded good results for non-aqueous solutions but the average absolute deviation (AAD) of viscosity calculation was as high as 13.7% for 12 binary aqueous solutions. Substantial improvement has been obtained as the augmented asymmetric mixing rule or the van Laar-type mixing rule was employed. The asymmetric models accompanying the determined binary interaction parameters could predict the viscosity of ternary aqueous solutions to within reasonable accuracy.

In addition to developing conventional equation-oriented models, an artificial neural computing technique has been applied recently by several investigators^{3, 6, 12)} to correlate thermophysical properties of fluids. Neural computing has several advantages over traditional digital computation such as faster speed of information processing, learning ability, fault tolerance and multi-output

ability. A neural model could be trained by using limited available data to predict the outputs (responses) corresponding to given inputs (stimuli) of interest. For example, all the individual binary information should be known prior to predicting a property of multicomponent mixtures with an equation-oriented model while it may not be necessary for the property prediction via a neural model. Neural computing is likely to be effective for developing a built-in model to calculate mixtures' properties. In the present article, the authors illustrate the capability of artificial neural networks for calculating the density and viscosity of polar liquid mixtures. The networks were trained with limited binary data, then applied to predict the properties of binary and ternary mixtures that were not included in the learning data base.

Since density and viscosity data of multicomponent polar solutions are not so plentiful in the literature, one binary and two ternary systems were determined experimentally in the present work. The excess properties were calculated from the measured data and then correlated using empirical equations. Besides the data of a butylamine + ethanol system reported in this article, a portion of published binary data was employed to train the artificial neural networks. Those learned networks appeared to predict satisfactorily the properties for the majority of ternary solutions being tested and the calculated results were comparable to those from the corresponding-states viscosity model of Lee and Wei⁹⁾ with asymmetric mixing rules for aqueous systems.

1. Experimental Section

Ethanol (99.8%), butylamine (99%) and benzylamine (98%) were supplied from Ferak, Germany. Water content in the amines is less than 0.5%. Deionized distilled

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Table 1. Density and Viscosity for Butylamine (1) + Ethanol(2)

x_1	303.15 K		313.15 K		323.15 K	
	ρ m [g·cm ⁻³]	η m [mPa·s]	ρ m [g·cm ⁻³]	η m [mPa·s]	ρ m [g·cm ⁻³]	η m [mPa·s]
0.0	0.7807	0.990	0.7722	0.834	0.7635	0.701
0.1	0.7783	0.949	0.7697	0.787	0.7607	0.669
0.2	0.7758	0.897	0.7668	0.746	0.7578	0.634
0.3	0.7715	0.831	0.7627	0.696	0.7528	0.585
0.4	0.7669	0.799	0.7577	0.668	0.7485	0.557
0.5	0.7618	0.724	0.7527	0.619	0.7434	0.524
0.6	0.7560	0.662	0.7468	0.558	0.7372	0.484
0.7	0.7505	0.613	0.7411	0.527	0.7319	0.453
0.8	0.7440	0.549	0.7349	0.471	0.7254	0.411
0.9	0.7386	0.489	0.7293	0.427	0.7191	0.371
1.0	0.7325	0.458	0.7232	0.398	0.7132	0.353

Table 2. Density and Viscosity for Butylamine (1) + Ethanol (2) + Water (3)

x_1	x_2	303.15 K		313.15 K		323.15 K	
		ρ m [g·cm ⁻³]	η m [mPa·s]	ρ m [g·cm ⁻³]	η m [mPa·s]	ρ m [g·cm ⁻³]	η m [mPa·s]
0.8	0.1	0.7490	0.602	0.7392	0.513	0.7298	0.444
0.6	0.3	0.7615	0.708	0.7523	0.604	0.7434	0.524
0.3	0.6	0.7803	0.971	0.7704	0.802	0.7610	0.669
0.1	0.8	0.7886	1.09	0.7798	0.896	0.7707	0.741
0.6	0.2	0.7670	0.829	0.7580	0.687	0.7485	0.574
0.4	0.4	0.7807	0.987	0.7717	0.799	0.7622	0.664
0.2	0.6	0.7942	1.19	0.7848	0.963	0.7756	0.783
0.6	0.1	0.7731	0.884	0.7639	0.722	0.7544	0.600
0.4	0.3	0.7885	1.12	0.7795	0.899	0.7702	0.735
0.3	0.4	0.7992	1.32	0.7904	1.05	0.7813	0.842
0.1	0.6	0.8116	1.42	0.8028	1.13	0.7938	0.906
0.4	0.2	0.7968	1.30	0.7878	1.03	0.7786	0.834
0.3	0.3	0.8056	1.39	0.7971	1.10	0.7878	0.882
0.2	0.4	0.8149	1.48	0.8062	1.16	0.7968	0.928
0.3	0.1	0.8271	1.76	0.8187	1.35	0.8095	1.06
0.2	0.2	0.8403	1.88	0.8316	1.43	0.8229	1.12
0.1	0.3	0.8555	1.93	0.8475	1.47	0.8385	1.15
0.1	0.1	0.8950	2.12	0.8877	1.59	0.8801	1.24

Table 3. Density and Viscosity for Butylamine (1) + Benzylamine (2) + Water (3)

x_1	x_2	303.15 K		313.15 K		323.15 K	
		ρ m [g·cm ⁻³]	η m [mPa·s]	ρ m [g·cm ⁻³]	η m [mPa·s]	ρ m [g·cm ⁻³]	η m [mPa·s]
0.1	0.1	0.9392	2.48	0.9317	1.88	0.9236	1.48
0.1	0.3	0.9566	2.77	0.9479	2.09	0.9390	1.64
0.1	0.6	0.9590	1.96	0.9505	1.58	0.9414	1.29
0.1	0.8	0.9552	1.52	0.9468	1.25	0.9380	1.06
0.2	0.2	0.9123	2.35	0.9039	1.80	0.8950	1.41
0.2	0.4	0.9270	2.01	0.9183	1.58	0.9095	1.27
0.2	0.6	0.9312	1.50	0.9228	1.27	0.9135	1.08
0.3	0.1	0.8657	1.91	0.8573	1.47	0.8482	1.17
0.3	0.3	0.8930	1.63	0.8843	1.30	0.8752	1.05
0.3	0.4	0.8891	1.47	0.8916	1.18	0.8823	0.983
0.3	0.6	0.9071	1.16	0.8984	0.974	0.8893	0.832
0.4	0.2	0.8570	1.38	0.8481	1.10	0.8387	0.906
0.4	0.3	0.8682	1.23	0.8596	1.01	0.8503	0.835
0.4	0.4	0.8764	1.11	0.8676	0.914	0.8585	0.771
0.6	0.1	0.8014	0.919	0.7924	0.760	0.7830	0.635
0.6	0.2	0.8176	0.850	0.8084	0.710	0.7990	0.609
0.6	0.3	0.8291	0.789	0.8202	0.674	0.8109	0.582
0.8	0.1	0.7723	0.622	0.7630	0.531	0.7533	0.460
0.20	0.02	0.8773	2.19	0.8695	1.67	0.8612	1.31
0.20	0.08	0.8928	2.28	0.8847	1.73	0.8759	1.36
0.05	0.02	0.9566	1.65	0.9509	1.30	0.9445	1.04
0.02	0.02	0.9802	1.33	0.9753	1.06	0.9694	0.863

Fig. 1 Kinematic viscosity for butylamine (1) + ethanol (2)

water with conductivity better than $2 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ was prepared in our laboratory. All the substances were used without further purification.

A detailed description for the measurements has been given elsewhere⁸). A HAAKE falling ball viscometer and pycnometers were utilized to measure the viscosity and density, respectively. Generally, the accuracy of measurements was better than $\pm 0.1\%$ for density, $\pm 1\%$ for viscosity, $\pm 0.1 \text{ K}$ for temperature, and $\pm 0.5 \text{ mg}$ for mixture preparation.

Tables 1-3 list the measured density and viscosity for butylamine + ethanol, butylamine + ethanol + water and butylamine + benzylamine + water, respectively. The kinematic viscosity of butylamine + ethanol varying with composition is illustrated in **Fig. 1** which shows the property decreasing linearly with the mole fraction of butylamine. Unlike aqueous solutions, this system displays no aggregate formation between dissimilar molecules. The contours of dynamic viscosity for the ternary system of butylamine + benzylamine + water at 303.15 K are presented in **Fig. 2**. The highest viscosity occurs at point A (i.e., the binary mixture of benzylamine + water with the mole fraction of benzylamine to be 0.333). Projections of the ridge of viscosity surface decline from point A toward point B along the segment AB and the lowest viscosity is located at the point of pure butylamine. The density surface of the same ternary solution is much simpler, varying linearly with composition.

2. Empirical Data Correlation

Excess volume and viscosity can be calculated from

$$Y^{\text{ex}} = Y_m - \sum_{i=1}^c (x_i Y_i) \quad (1)$$

where Y represents molar volume and dynamic viscosity. **Fig. 3** exhibits negative excess volumes for butylamine + ethanol over the entire composition range. The excess properties of this binary system were correlated by a

Fig. 2 Contours of viscosity surface for butylamine (1) + benzylamine (2) + water (3) at 303.15 K

Fig. 3 Excess volume for butylamine (1) + ethanol (2)

Redlich-Kister type model, *i.e.*,

$$Y^{ex} = x_1 x_2 \sum_{j=0}^3 A_j (x_1 - x_2)^j \quad (2)$$

and those of the ternary systems were fitted to the following simple equation:

$$Y^{ex} = Y_{12}^{ex} + Y_{13}^{ex} + Y_{23}^{ex} + B x_1 x_2 x_3 \quad (3)$$

where Y_{ij}^{ex} was calculated from the corresponding binary data⁷⁾. The temperature-specific parameter, B , was determined from the ternary data. **Table 4** lists the optimal coefficients of Eqs. (2) and (3) for the investigated systems. It is found that Eq. (2) correlates with binary density and viscosity data to within experimental accuracy. Equation (3) is also adequate enough for correlating the ternary density data but it is not so successful for viscosity. A greater number of coefficients seems to be required for the butylamine + benzylamine + water system.

Table 4. Coefficients of Eqs. (2) and (3)

density	T [K]	A_0	A_1	A_2	A_3	B	AAD (%) ^a
butylamine	303.15	-4.7158	0.9029	0.1997	-1.0857	—	0.02
+ ethanol	313.15	-5.0104	1.0046	-0.6951	0.0420	—	0.02
	323.15	-5.1494	0.2365	0.1143	0.9710	—	0.03
butylamine	303.15	—	—	—	—	6.1802	0.12
+ ethanol	313.15	—	—	—	—	5.4611	0.11
+ water	323.15	—	—	—	—	14.3924	0.19
butylamine	303.15	—	—	—	—	3.5510	0.15
+ benzylamine	313.15	—	—	—	—	-3.9159	0.16
+ water	323.15	—	—	—	—	-2.8385	0.12
viscosity	T (K)	A_0	A_1	A_2	A_3	B	AAD(%) ^a
butylamine	303.15	-0.0140	-0.0399	-0.2089	-0.1474	—	0.77
+ ethanol	313.15	-0.0123	-0.0322	-0.2099	0.0092	—	0.71
	323.15	-0.0179	0.0456	-0.0933	-0.2732	—	0.50
butylamine	303.15	—	—	—	—	-4.1050	5.67
+ ethanol	313.15	—	—	—	—	-3.4095	4.67
+ water	323.15	—	—	—	—	-1.8680	3.83
butylamine	303.15	—	—	—	—	-22.4418	13.60
+ benzylamine	313.15	—	—	—	—	-20.1251	18.06
+ water	323.15	—	—	—	—	-14.6436	16.29

^a

$$AAD = \frac{100}{n} \sum_{k=1}^n \left| \frac{Y^{cal} - Y^{exp}}{Y^{exp}} \right|_k$$

where Y represents density and viscosity.

Table 5. Network Structures

	network-A	network-B	network-C
input layer	T, x_1, x_2, x_3	$T, x_1, \dots, x_7$	$T, x_1, \dots, x_{15}$
hidden layer-1	10	15	32
hidden layer-2	4	7	—
output layer	ρ, m, η, m	ρ, m, η, m	η, m
transfer function	sigmoid	sigmoid	sigmoid

3. Data Correlation with Artificial Neural Networks

By using the Professional II/Plus package (Neural Ware, Inc., USA), three neural networks were developed for calculating the density and viscosity of polar liquid mixtures with emphasis on aqueous solutions. The network structures are summarized in **Table 5**. In these networks, temperature is an input variable to specify the condition of solutions. Mole fraction of components is used in this study to characterize the mixtures and each compound corresponds to a specific input node. Meanwhile, the sigmoid transfer function is assigned to all processing units and the back-propagation algorithm with the generalized delta rule is utilized in the learning processes.

3.1 Network-A

Among the three neural models, network-A demonstrates the validity of the neural computing technique for predicting the properties of butylamine + benzylamine + water system based on their binary data. It means that the response surfaces over the entire ternary composition range have to be predicted according to the properties at three binary boundaries via the neural model. As a consequence, an acceptable model should quantitatively take molecular interactions into account through the network's connections in order to make a good prediction. Since no general rules

Fig. 4 Learning history of network-A

can be followed, the network structure is determined empirically. Network-A given in Table 5 is one of the best combinations being investigated by the authors. This network includes four input nodes corresponding to temperature of solution (T) and mole fractions of butylamine, benzylamine and water (x_1 , x_2 and x_3), two hidden layers with ten and four processing elements, respectively and two output nodes providing density and dynamic viscosity responses. Binary experimental data of butylamine + water, benzylamine + water and butylamine + benzylamine⁷⁾ were used as training data and the third mole fraction input was set to zero for each binary system. The training process was paused after certain learning-cycles (*i.e.* time-steps) to check the accuracy of calculation. Figure 4 shows the learning history. As the authors expected, the calculated results for density are much better than those for viscosity since the response surfaces of viscosity are much more complicated than those of density as noted earlier. Network-A predicts the ternary density to an AAD of 2% only after 20 time-steps while it needs at least 100 time-steps for reducing the predicted AAD to 10% for the ternary viscosity. The learning process was terminated finally at 291 time-steps. This trained network correlates the binary data to an AAD of 0.43% for density and 4.28% for viscosity and predicts the ternary density and viscosity to 0.68% (AAD) and 3.96% (AAD), respectively. In comparison with the calculated viscosities of the butylamine + benzylamine + water system resulting from the empirical correlation (see Table 4), the viscosity prediction from this neural model is much better.

3.2 Network-B

Promising results from the above illustration encouraged the authors to develop two other neural models that can treat a greater number of liquids. Network-B was also designed for calculating density and viscosity, simultaneously. Owing to the limitation of aqueous data, seven highly polar liquids (methanol, ethanol, 1-propanol, acetone, butylamine, benzylamine and water) were selected as the model components for network-B. The structure of

network-B was given in Table 5. There are eight nodes in the input layer corresponding to temperature and mole fractions of the selected compounds, two hidden layers with 15 and 7 processing elements and two nodes in the output layer to give calculated density and viscosity. The network was trained by using 353 binary data including 12 binary systems. After 720 learning-cycles, the network correlates the binary density to 0.32% (AAD) and viscosity to 2.88% (AAD). Table 6 indicates that the learning is generally satisfactory. Results for the mixture containing acetone, however, are not so accurate. Fewer data points of acetone-containing mixtures adopted in the learning data base could be the reason. A good agreement between the predicted and experimental values is obtained for acetone-free ternary systems as shown in Table 7. Each binary pair involving in those tested ternary systems was included in the learning data base although it may not be necessary. Basically, this network is developed for calculating the properties of multicomponent mixtures containing up to seven components. However, multicomponent experimental data are so scarce that the validity of the network was tested here up to ternary mixtures.

3.3 Network-C

Comparing the results from network-B with those from network-A, it was noted that the accuracy of calculations could be retained even though the number of liquids was increased. The number of compounds was further extended to 15 in network-C that was developed for calculating viscosity only due to lack of density data for several binary systems. As presented in Table 5, the network has 16 input nodes including temperature and the mole fractions of methanol, ethanol, 1-propanol, *i*-propanol, *i*-butanol, acetone, 2-picoline, acetonitrile, acetic acid, propionic acid, *n*-butyric acid, 1,4-dioxane, butylamine, benzylamine and water. The single hidden layer contains 32 processing units and the only output node corresponds to viscosity. This network was trained by 583 binary data (including 20 binary systems) and terminated after 1063 learning-cycles. As shown in Table 6, network-C correlates the training data to an AAD of 3.82%. This model quantitatively predicts the viscosity of methanol + *i*-propanol and ethanol + *i*-propanol. These two binary systems were not included in the training data base. It appears that the neural model could predict the property of new combination systems by using the knowledge of given binary systems while conventional models usually fail. Moreover, the network predicts the viscosity of ternary aqueous solutions to an AAD of 4.30% as given in Table 7.

Lee and Wei⁹⁾ reported that viscosity calculations can be improved substantially by using their corresponding-states model with the asymmetric mixing rules (see Appendix) for aqueous solutions. For comparison purposes, results from the corresponding-states model are also compiled in Tables 6 and 7, respectively. It appears that the neural models are comparable to the corresponding-states model for both binary and ternary aqueous solutions.

Table 6. Calculated Results from the Networks and the Corresponding-States Model for Binary Solutions

AAD (%)									
mixture	<i>n</i>	network-A		network-B		network-C	CSM ^a		source
		ρ m	η m	ρ m	η m	η m	AAMR	VLMR	
methanol+water	49	—	—	0.27	2.96	3.02	1.99	1.61	10)
ethanol+water	47	—	—	0.20	2.71	2.95	4.55	2.14	2)
1-propanol+water	10	—	—	0.26	2.53	2.42	8.57	3.25	2)
<i>i</i> -propanol+water	27	—	—	—	—	3.92	11.79	6.77	3)
<i>i</i> -butanol+water	5	—	—	—	—	8.22	8.48	7.71	15)
acetone+water	9	—	—	0.46	8.47	11.20	2.06	6.57	11)
2-picoline+water	27	—	—	—	—	3.72	3.71	3.04	8)
acetonitrile+water	9	—	—	—	—	4.85	1.35	3.64	3)
acetic acid+water	90	—	—	—	—	3.67	7.50	7.73	3)
propionic acid+water	9	—	—	—	—	3.45	7.37	7.64	3)
<i>n</i> -butyric acid+water	9	—	—	—	—	3.06	9.98	5.25	3)
1, 4-dioxane+water	54	—	—	—	—	3.08	4.02	1.75	3)
butylamine+water ^b	33	0.62	6.02	0.51	3.08	4.15	5.60	8.75	7)
benzylamine+water ^c	33	0.36	3.54	0.21	3.09	7.26	8.27	7.72	7)
methanol+ethanol	63	—	—	0.33	1.13	1.39	—	—	2)
methanol+1-propanol	12	—	—	0.25	1.66	1.81	—	—	2)
methanol+acetone	15	—	—	0.27	8.33	13.71	—	—	11)
ethanol+1-propanol	12	—	—	0.55	1.14	0.61	—	—	2)
butylamine+ethanol	33	—	—	0.40	2.40	4.47	—	—	this work
butylamine+benzylamine	37	0.34	3.42	0.32	3.79	3.39	—	—	7)
methanol+ <i>i</i> -propanol ^d	12	—	—	—	—	5.99	—	—	17)
ethanol+ <i>i</i> -propanol ^d	8	—	—	—	—	1.72	—	—	17)

^aCSM : Corresponding-State Model⁹⁾

AAMR : Augmented Asymmetric Mixing Rule

VLMR : van Laar-type Mixing Rule

^bAAMR : $k_{12} = -0.0448$, $A_{1w} = 932.1$; VLMR : $K_{12} = -1.4327$, $K_{21} = -0.1381$ ^cAAMR : $k_{12} = -0.0702$, $A_{1w} = 653.7$; VLMR : $K_{12} = -1.6780$, $K_{21} = -0.1041$ ^dSystems that were not included in the training data base.**Table 7.** Calculated Results from the Networks and the Corresponding-States Model for Ternary Solutions

AAD (%)									
mixture	<i>n</i>	network-A		network-B		network-C	CSM		source
		ρ m	η m	ρ m	η m	η m	AAMR	VLMR	
methanol+ethanol+water	69	—	—	0.23	3.36	3.91	4.74	8.00	2)
methanol+1-propanol+water	24	—	—	0.22	2.27	2.44	3.71	6.58	2)
methanol+acetone+water	28	—	—	0.18	7.35	10.63	1.96	6.10	11)
ethanol+1-propanol+water	24	—	—	0.10	2.32	1.98	5.31	5.97	2)
butylamine+benzylamine+water	66	0.68	3.96	0.55	3.78	2.91	3.11	6.84	this work
butylamine+ethanol+water	54	—	—	0.36	5.79	5.22	6.70	4.32	this work
methanol+ethanol+1-propanol	24	—	—	0.16	0.94	1.32	—	—	2)
methanol+ethanol+ <i>i</i> -propanol	12	—	—	—	—	8.22	—	—	18)

Conclusion

New density and viscosity data were reported for the liquid mixtures of butylamine + ethanol, butylamine + ethanol + water and butylamine + benzylamine + water at temperatures of 303.15 - 333.15 K. It was apparent that no aggregate formed between butylamine and ethanol molecules. The illustrative examples showed that the artificial neural networks developed in the present study could calculate satisfactorily the density and viscosity for the binary polar mixtures, and predict quantitatively properties for the majority of the ternary systems being tested. Regarding the viscosity calculation for aqueous solutions, the neural models were comparable to the corresponding-states model of Lee and Wei⁹⁾.

Appendix

Corresponding-States Viscosity Model of Lee and Wei⁹⁾

$$\eta_r(T_r, P_r) = \eta_{r1} + \frac{\alpha - \alpha_1}{\alpha_2 - \alpha_1} (\eta_{r2} - \eta_{r1}) + \beta^* \left\{ \eta_{r3} - \left[\eta_{r1} + \frac{\alpha_3 - \alpha_1}{\alpha_2 - \alpha_1} (\eta_{r2} - \eta_{r1}) \right] \right\} \quad (\text{a1})$$

with

$$\eta_r = \ln \left(\frac{\eta}{\eta^*} + 1 \right) \quad (\text{a2})$$

$$\eta^* = \frac{10^3 M^{1/2} P_c^{2/3}}{(RT_c)^{1/6} N_a^{1/3}} \quad (\text{a3})$$

$$T_r = T / (T_c \theta) \quad (\text{a4})$$

$$P_r = P / P_c \quad (\text{a5})$$

where the reduced viscosity of the i th reference fluid (oxygen, octane, or water) was expressed as

$$\eta_{ri} = D_0 + D_1 / T_r + D_2 T_r + D_3 T_r^2 + D_4 P_r + D_5 P_r^{1/2} + D_6 T_r P_r \quad (\text{a6})$$

The optimal coefficients, D_0 - D_6 , for each reference fluid have been given elsewhere⁹. For mixture calculation, the mixing rules are defined as follows:

$$Q_m = \sum_{i=1}^c \sum_{j=1}^c x_i x_j Q_{ij} \quad (\text{a7})$$

where Q represents M , P_c , α , θ , and β^* . The values of M_{ij} , α_{ij} , and β_{ij}^* are computed from the arithmetic average of the pure components,

$$Q_{ij} = 0.5 (Q_i + Q_j) \quad (\text{a8})$$

whereas those of P_{cij} and θ_{ij} are evaluated from the geometric average.

$$Q_{ij} = (Q_i Q_j)^{1/2} \quad (\text{a9})$$

As noted earlier, asymmetric T_{cm} should be used for aqueous systems. Two types of asymmetric mixing rule for T_{cm} are adopted. One is the van Laar-type mixing rule, which is given by

$$T_{cm} = \left\{ \sum_{i=1}^c \sum_{j=1}^c x_i x_j (1 - k_{ij}) [(T_c \theta)_i (T_c \theta)_j]^{1/2} \right\} / \theta_m \quad (\text{a10})$$

with

$$k_{ij} = \frac{K_{ij} K_{ji}}{x_i K_{ij} - x_j K_{ji}} \quad (\text{a11})$$

and

$$x_i' = x_i / (x_i + x_j) \quad (\text{a12})$$

The other is the augmented asymmetric mixing rule, which is defined as

$$T_{cm} = \left\{ \sum_{i=1}^c \sum_{j=1}^c x_i x_j (1 - k_{ij}) [(T_c \theta)_i (T_c \theta)_j]^{1/2} + \sum_{i \neq w}^c A_{iw} (1 - x_w) x_w^3 \right\} / \theta_m \quad (\text{a13})$$

For a binary aqueous system, there are two adjustable interaction constants in both mixing rules, i.e. K_{12} and K_{21} in the van Laar-type mixing rule, k_{12} and A_{1w} in the augmented asymmetric mixing rule.

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Nomenclature

AAD	= average absolute deviation	[%]
A_j	= coefficients in Eq. (2)	
A_{iw}	= binary interaction parameter	
B	= coefficient in Eq. (3)	
c	= number of component	
D_0 - D_6	= coefficient in Eq. (a6)	
k_{ij}	= binary interaction parameter	
K_{ij} , K_{ji}	= binary interaction parameters	
M	= molecular weight	[g·mol ⁻¹]
N_a	= Avogadro's number	[kmol ⁻¹]
n	= number of data points	
P	= pressure	[Pa]

Q	= general variable	
R	= gas constant	[J·kmol ⁻¹ ·K ⁻¹]
T	= temperature	[K]
V	= molar volume	[cm ³ ·mol ⁻¹]
x	= mole fraction	
Y	= general variable	

α	= radius of gyration	[nm/10]
β^*	= polar/associated parameter	
η	= dynamic viscosity	[mPa·s]
η^*	= characteristic viscosity	[mPa·s]
θ	= energy correction factor	
ν	= kinematic viscosity	[cSt]
ρ	= density	[g·cm ⁻³]

<Superscript>

<i>cal</i>	= calculated value
<i>ex</i>	= excess property
<i>exp</i>	= experimental value

<Subscript>

<i>c</i>	= critical property
<i>i</i>	= component <i>i</i>
<i>ij</i>	= binary system containing <i>i</i> and <i>j</i> components
<i>j</i>	= component <i>j</i>
<i>m</i>	= mixture
<i>r</i>	= reduced property
<i>ri</i>	= <i>i</i> th reference fluid
<i>w</i>	= water

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