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Estimation of the entropy of vaporization at the normal boiling point for azeotropic mixtures containing water, alcohol or acetic acid

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Abstract

The entropy of vaporization at the normal boiling point has been estimated for binary and ternary azotropic mixtures containing water, alcohol or acetic acid. For this purpose, the Lee–Kesler correlation, developed originally for pure substances, is used with the appropriate mixing rules to estimate the heat of vaporization of the mixtures. Estimations for the entropy of vaporization of the 97 binary and 78 ternary mixtures are expressed as function of the ratio of the normal boiling point to average molecular weight. These expressions predict the entropy of vaporization satisfactorily, with less than 5% average deviation.

Keywords: Entropy of vaporization; Azeotropic mixtures; Heat of vaporization

1. Introduction

The studies such as the entropy of association [1], the entropy of hydration [2] in mixtures, and the entropy of vaporization [3] for pure substances show that the aspect of entropy is an important tool to understand the behavior of the mixtures and pure substances. In another study, the hydrogen-bond enthalpies of monohydric alcohols are estimated from the entropy of vaporization [4]. Behavior of the azeotropic mixtures is of great interest as they are treated as pure substances, and they may be used to test the thermodynamic models [5]. It is common to apply the Clausius–Clapeyron equation to correlate the heat of vaporization for azeotropic mixtures [6].

In this study, the entropy of vaporization for azeotropic mixtures at the normal boiling point is estimated for the binary and ternary azeotropic mixtures using the correlation for the heat of vaporization developed for a pure substance. These estimations have been fitted into simple correlation equations in terms of the boiling point and averaged molecular weight.

2. Heat of vaporization

Tamir [7] tested the three available correlations, originally developed for pure-substances, and suggested that with the appropriate mixing rules such correlations can predict the heat of vaporization for azeotropic mixtures. He recommended the Lee–Kesler correlation which produced an average deviations of 5.1% for 103 binary azeotropes and of 2.6% for 13 ternary azeotropes in estimations of the heat of vaporization ΔH_v. Therefore, the values of ΔH_v for azeotropic mixtures were estimated from the Lee–Kesler

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correlation given by [8]

$$\Delta H_v = RT_c[6.09648 - 1.2886T_r + 1.0167T_r^7 + \omega(15.6875 - 13.4721T_r + 2.615T_r^7)] \quad (1)$$

where T_r is reduced temperature (T_b/T_c), T_b is the normal boiling point in Kelvin, $R = 1.987$ cal mol^{-1} K^{-1} and ΔH_v is in cal mol^{-1}. The critical temperature, T_c and the acentric factor ω of the mixture are obtained from the following mixing rules using the azeotropic compositions x_i [7,8]

$$T_c = \sum_{i=1}^{c} \phi_i T_{ci} \quad (2)$$

where

$$\phi_i = \frac{x_i v_{ci}}{\sum_{i=1}^{c} x_i v_{ci}} \quad (3)$$

$$\omega = \sum_{i=1}^{c} x_i \omega_i \quad (4)$$

Here c is the number of components. The critical temperature T_{ci}, the critical volume v_{ci}, and acentric factor ω_i of the pure components are taken from Reid et al. [8].

3. Entropy of vaporization

The entropy of vaporization ΔS_v is proportional to the ratio of the degree of randomness in the vapor and the liquid phases. The values of ΔS_v for a pure substance consists of three contributions due to changes in translational, rotational and conformational motion of the molecules [3]

$$\Delta S_v = \Delta S_{trans} + \Delta S_{rot} + \Delta S_{conf} \quad (5)$$

The translational change is the largest contribution to the entropy of vaporization, while the conformational and rotational restrictions in the liquid also contribute to the total entropy [3]. These restrictions are a consequence of molecular structure, and their contributions to the total entropy in a mixture should be more considerable.

Beside Trouton's rule, several methods to estimate the entropy of vaporization of the pure substances are described and tested by Reid et al. [8]. A group contribution method based on molecular structure alone [9,10], and an expression in terms of molecular flexibility and hydrogen bonding [3] are also suggested. Vetere expressed ΔS_v in terms of T_b and molecular weight M, and suggested the following expression for pure substances of alcohols, acids and methylamine [8]

$$\Delta S_v = 81.119 + 13.083 \log T_b - 25.769\frac{T_b}{M} + 0.146528\frac{T_b^2}{M} - 2.1362\times10^{-4}\frac{T_b^3}{M} \quad (6)$$

This equation predicts ΔH_v within 5% of the experimental data [8].

In order to estimate the entropy of vaporization for azeotropic mixtures, data of compositions and the normal boiling points of 97 binary and 78 ternary systems containing water, alcohol or acetic acid were compiled from Horsley [11]. These type of mixtures have the hydrogen bonding, and hence relatively high values of ΔS_v. The values of ΔH_v for the azeotropic mixtures were estimated from Eq. (1), and the entropy of vaporization was obtained by

$$\Delta S_v = \frac{\Delta H_v}{T_b} \quad (7)$$

Here T_b is the normal boiling point of the azeotropes. The estimations of the entropy of vaporization were fitted to the correlation equations in terms of the ratio of the normal boiling point in Kelvin to the average molecular weight of the mixture, M_{av}

$$\Delta S_v = 84.807 + 11.740 \ln\left(\frac{T_b}{M_{av}}\right) \quad \text{for 97 binary azeotropes} \quad (8)$$

$$\Delta S_v = 83.710 + 12.954 \ln\left(\frac{T_b}{M_{av}}\right) \quad \text{kern1}pt \text{ for 78 ternary azeotropes} \quad (9)$$

Where M_{av}, ($M_{av} = \sum_{i=1}^{c} x_i M_i$) was obtained from the azeotropic compositions x_i and molecular weights of pure substances M_i, with c showing the number of components.

4. Results and discussion

Using Eqs. (1) and (7), the entropy of vaporization at the normal boiling point was estimated for 97 binary

Table 1
Entropy of vaporization at the normal boiling point for binary azeotropic mixtures

	System	x_1	T_b (K)	ΔH_v (J mol^{-1})	ΔS_v (J mol^{-1} K^{-1})	Eq. (8) (D_1)	Eq. (6) (D_2)
1	Water(1)-propyl alcohol(2)	0.568	360.1	40675.7	112.9	1.1	5.4
2	Water(1)-2-butanone(2)	0.338	346.5	35074.6	101.2	5.4	8.9
3	Water(1)-sec-butanol(2)	0.601	360.1	39273.9	109.0	1.4	0.8
4	Water(1)-tert-butanol(2)	0.354	353.0	37916.8	107.4	0.6	2.7
5	Water(1)-carbon disulfide(2)	0.108	315.7	29907.2	94.7	7.8	15.4
6	Water(1)-chloroform(2)	0.160	329.2	32155.3	97.6	0.8	14.2
7	Water(1)-ethanol(2)	0.096	351.3	40683.6	115.8	6.4	6.7
8	Water(1)-nitromethane(2)	0.511	356.7	39643.5	111.1	0.3	2.8
9	Water(1)-1-hexene(2)	0.224	330.8	31486.6	95.1	7.7	15.8
10	Water(1)-hexane(2)	0.221	334.7	31915.8	95.3	7.6	15.8
11	Water(1)-1-heptene(2)	0.486	350.1	35838.1	102.3	3.3	8.2
12	Water(1)-heptane(2)	0.452	352.3	35736.3	101.4	3.6	9.3
13	Water(1)-1-octene(3)	0.715	361.1	38904.7	107.7	1.5	1.1
14	Water(1)-octane(2)	0.685	362.7	38915.5	107.3	1.2	1.9
15	Water(1)-1-nonene(2)	0.858	367.6	41158.6	111.9	1.0	5.8
16	Water(1)-nonane(3)	0.970	367.9	42911.1	116.6	1.6	15.3
17	Water(1)-1-decene(3)	0.933	369.8	42849.8	115.8	0.1	12.4
18	Water(1)-undecane(2)	0.995	372.0	43740.6	117.6	2.3	19.2
19	Water(1)-dodecane(2)	0.998	372.6	43765.5	117.4	2.7	19.5
20	Water(1)-acetonitrile(2)	0.307	349.6	36258.3	103.7	8.5	3.9
21	Water(1)-isopropyl alcohol(2)	0.313	353.2	34930.6	98.8	9.6	10.5
22	Water(1)-ethyl acetate(2)	0.312	343.5	34821.8	101.3	2.8	9.6
23	Water(1)-1,2 dichloroethane(2)	0.357	345.4	36707.6	106.2	2.7	4.9
24	Water(1)-butanol(2)	0.753	365.8	41464.4	113.3	0.1	7.3
25	Water(1)-pyridine(2)	0.768	367.1	41514.4	113.1	0.3	7.1
26	Water(1)-cyclohexane(2)	0.300	342.6	33703.7	98.3	6.1	12.5
27	Water(1)-toluene(2)	0.444	357.2	38137.5	106.7	0.8	3.6
28	Water(1)-benzene(2)	0.296	342.4	34421.9	100.5	4.6	10.1
29	Water(1)-ethyacrylate(2)	0.495	354.2	35521.8	100.2	5.5	10.2
30	Carbon tetrachloride(1)-sec-butanol(2)	0.854	347.7	32246.6	92.7	2.6	20.0
31	Carbon tetrachloride(1)-tert-butanol(2)	0.702	344.2	32452.0	94.2	1.9	18.3
32	Carbon tetrachloride(1)-propyl alcohol(2)	0.820	346.5	32116.2	92.6	3.0	20.0
33	Carbon disulfide(1)-methanol(2)	0.508	312.9	35438.7	113.2	7.9	4.2
34	Carbon disulfide(1)-ethanol(2)	0.860	315.7	31049.4	98.3	3.8	11.9
35	Chloroform(1)-methanol(2)	0.651	326.5	34713.4	106.3	6.2	5.1
36	Chloroform(1)-ethanol(2)	0.837	332.5	33054.9	99.4	1.3	12.6
37	Nitromethane(1)-methanol(2)	0.050	337.5	39338.2	116.5	4.6	8.8
38	Nitromethane(1)-acetic acid(2)	0.959	374.3	37158.7	99.2	6.8	10.3
39	Nitromethane(1)-isopropyl alcohol(2)	0.279	352.4	40136.6	113.9	8.3	3.3
40	Nitromethane(1)-butanol(2)	0.739	370.9	38845.4	104.7	0.6	5.3
41	Nitromethane(1)-sec-butanol(2)	0.508	364.2	38560.4	105.8	1.2	4.7
42	Nitromethane(1)-tert-butanol(2)	0.364	352.5	38324.6	108.7	4.8	2.3
43	Methanol(1)-acetonitrile(2)	0.231	336.6	36717.8	109.1	1.0	0.5
44	Methanol(1)-acrylonitrile(2)	0.724	334.5	38605.1	115.4	5.0	7.0
45	Methanol(1)-acetone(2)	0.198	328.6	33217.7	101.1	5.1	8.7
46	Methanol(1)-ethyl acetate(2)	0.684	335.4	37992.7	113.3	6.0	3.5
47	Methanol(1)-1-hexene(2)	0.408	321.3	34395.1	107.0	3.0	3.0
48	Methanol(1)-hexane(2)	0.491	322.6	35542.0	110.1	5.5	0.1
49	Methanol(1)-toluene(2)	0.883	348.1	39778.0	114.2	3.7	5.6
50	Acetonitrile(1)-ethanol(2)	0.469	345.6	38739.3	112.1	2.9	2.8
51	Acetonitrile(1)-isopropyl alcohol(2)	0.613	347.6	37498.2	107.8	0.1	1.8
52	Acetonitrile(1)-propyl alcohol(2)	0.790	354.3	36511.7	103.0	5.9	6.1

Table 1 (*Continued*)

	System	x_1	T_b (K)	ΔH_v (J mol^{-1})	ΔS_v (J mol^{-1} K^{-1})	Eq. (8) (D_1)	Eq. (6) (D_2)
53	1,2 dichloroethane(1)-ethanol(2)	0.804	343.6	35266.1	102.6	4.2	7.4
54	1,2 dichloroethane(1)-isopropyl alcohol(2)	0.655	347.8	37230.8	107.0	1.1	2.6
55	Acetic acid(1)-butanol(2)	0.482	393.4	41773.9	106.1	0.6	1.9
56	Acetic acid(1)-chlorobenzene(2)	0.725	387.8	41422.9	106.8	2.6	2.6
57	Acetic acid(1)-toluene(2)	0.375	373.7	38108.1	101.9	0.9	8.8
58	Acetic acid(1)-heptane(2)	0.255	368.1	35563.5	96.6	4.7	14.9
59	Acetic acid(1)-octane(2)	0.678	378.2	40100.3	106.0	2.6	4.4
60	Acetic acid(1)-nonane(2)	0.826	385.9	41737.9	108.1	3.6	1.2
61	Acetic acid(1)-decane(2)	0.902	389.9	42187.6	108.2	2.9	0.4
62	Acetic acid(1)-undecane(2)	0.980	390.8	41826.0	107.0	0.6	0.9
63	Ethanol(1)-acrylonitrile(2)	0.445	343.9	38065.2	110.6	3.2	0.8
64	Ethanol(1)-2-butanone(2)	0.500	347.1	37980.2	109.4	3.8	1.1
65	Ethanol(1)-ethyl acetate(2)	0.462	344.9	37557.3	108.8	5.1	2.2
66	Ethanol(1)-benzene(2)	0.448	341.4	37647.5	110.3	5.7	0.5
67	Ethanol(1)-1-hexene(2)	0.281	327.9	33746.5	102.9	0.5	8.0
68	Ethanol(1)-hexane(2)	0.332	331.8	34691.9	104.5	1.9	6.5
69	Isopropyl alcohol(1)-2-butanone(2)	0.361	351.0	36655.8	104.4	0.3	6.6
70	Isopropyl alcohol(1)-ethyl acetate(2)	0.328	349.0	36370.7	104.2	1.9	7.3
71	Isopropyl alcohol(1)-benzene(2)	0.393	345.0	36768.5	106.5	3.1	4.6
72	Isopropyl alcohol(1)-cyclohexane(2)	0.397	342.5	36548.6	106.7	3.9	4.6
73	Isopropyl alcohol(1)-1-hexene(2)	0.187	332.3	32625.8	98.1	3.4	13.1
74	Isopropyl alcohol(1)-hexane(2)	0.300	335.8	34308.1	102.1	0.2	9.2
75	Propyl alcohol(1)-benzene(2)	0.209	350.2	34791.6	99.3	3.6	12.0
76	Propyl alcohol(1)-cyclohexane(2)	0.259	347.4	34947.7	100.6	1.7	10.9
77	propyl alcohol(1)-hexane(2)	0.056	338.8	31597.3	93.2	7.8	18.3
78	Propyl alcohol(1)-toluene(2)	0.617	365.6	40821.5	111.6	7.8	0.8
79	Propyl alcohol(1)-heptane(2)	0.470	357.7	38476.8	107.6	5.3	3.9
80	Propyl alcohol(1)-m-xylene(2)	0.965	370.2	42002.0	113.4	7.6	3.5
81	Propyl alcohol(1)-*p*-xylene(2)	0.954	370.0	42116.0	113.8	8.0	3.8
82	Butanol(1)-pyridine(2)	0.704	391.7	41349.7	105.6	1.4	3.5
83	Butanol(1)-chlorobenzene(2)	0.659	388.4	42272.3	108.8	6.4	1.3
84	Butanol(1)-cyclohexane(2)	0.106	352.9	32924.7	93.2	8.5	18.3
85	Butanol(1)-toluene(2)	0.369	378.6	38824.5	102.5	0.2	8.2
86	Butanol(1)-1-heptene(2)	0.165	363.1	35873.2	98.7	1.8	13.0
87	Butanol(1)-heptane(2)	0.229	367.1	36307.1	98.9	1.8	12.8
88	Butanol(1)-octane(2)	0.606	383.3	41268.9	107.7	5.8	3.0
89	Butanol(1)-nonane(2)	0.813	389.0	43278.0	111.2	8.4	1.2
90	Sec-butanol(1)-benzene(2)	0.161	351.6	33749.7	95.9	6.6	15.4
91	Sec-butanol(1)-cyclohexane(2)	0.199	349.1	33662.4	96.4	5.3	15.2
92	Sec-butanol(1)-hexane(2)	0.092	340.3	31782.8	93.3	7.7	18.3
93	Sec-butanol(1)-toluene(2)	0.603	368.4	39001.7	105.9	3.3	5.3
94	Tert-butanol(1)-benzene(2)	0.378	347.1	35534.1	102.4	0.2	9.0
95	Tert-butanol(1)-cyclohexane(2)	0.400	344.4	35516.4	103.1	1.2	8.4
96	Tert-butanol(1)-hexane(2)	0.247	336.8	33277.9	98.8	2.4	12.7
97	Tert-butanol(1)-heptane(2)	0.688	351.1	38399.8	109.4	7.5	2.2
					105.3[a]	4.6[b]	7.6[b]

[a] Average value: $\Delta S_{v,av}$.

[b] Average deviation ($(1/n)\sum_{j=1}^{n} D_j$); $D_1 = |\Delta S_v - \Delta S_v \text{ (Eq. 8)}|$; $D_2 = |\Delta S_v - \Delta S_v \text{ (Eq.(6))}|$; n: number of systems.

and 78 ternary azeotropic mixtures. The estimated values of ΔS_v were compared with those predicted values from the correlations of Eqs. (8) and (9), and Eq. (6) which was used for both the binary and ternary azeotropes. Tables 1 and 2 show the estimations as well as the absolute deviations D_1 and D_2 obtained

Table 2
Entropy of vaporization at the normal boiling point for ternary azeotropic mixtures

	System	x_1	x_2	T_b (K)	ΔH_v (J mol^{-1})	ΔS_v (J mol^{-1} K^{-1})	Eq. (9) (D_1)	Eq. (6) (D_2)
1	Water(1)-carbon tetrachloride(2)-ethanol(3)	0.194	0.576	334.9	35563.0	106.2	7.2	5.8
2	Water(1)-carbon tetrachloride(2)-propyl alcohol(3)	0.276	0.542	338.5	36387.7	107.4	7.9	4.5
3	Water(1)-carbon tetrachloride(2)-2-butanone(3)	0.173	0.506	338.8	33275.8	98.2	0.8	13.6
4	Water(1)-carbon tetrachloride(2)-sec-butanol(3)	0.255	0.670	338.1	34945.6	103.3	5.4	8.9
5	Water(1)-carbon tetrachloride(2)-tert-butanol(3)	0.194	0.624	337.8	33740.0	99.8	1.9	12.1
6	Water(1)-carbon disulfide(2)-ethanol(3)	0.062	0.861	314.4	30701.9	97.6	5.5	13.0
7	Water(1)-carbon disulfide(2)-acetone(3)	0.031	0.683	311.2	30173.5	96.9	6.2	13.0
8	Water(1)-chloroform(2)-methanol(3)	0.066	0.698	325.4	34088.7	104.7	4.6	6.7
9	Water(1)-chloroform(2)-ethanol(3)	0.129	0.795	328.4	32954.9	100.3	1.3	11.0
10	Water(1)-chloroform(2)-acetone(3)	0.163	0.353	333.5	32303.9	96.8	6.5	14.0
11	Water(1)-nitromethane(2)-isopropyl alcohol(3)	0.176	0.278	351.1	39705.5	113.0	4.8	3.0
12	Water(1)-nitromethane(2)-propyl alcohol(3)	0.417	0.393	355.4	39860.7	112.1	1.0	3.2
13	Water(1)-nitromethane(2)-3-pentanone	0.492	0.137	355.5	38029.4	106.9	2.3	2.6
14	Water(1)-nitromethane(2)-1-hexene(3)	0.217	0.141	328.6	32367.4	98.4	5.6	11.9
15	Water(1)-nitromethane(2)-hexane(3)	0.243	0.171	330.0	33118.6	100.3	4.3	9.9
16	Water(1)-nitromethane(2)-1-heptene(3)	0.416	0.239	342.8	36690.7	107.0	0.2	3.3
17	Water(1)-nitromethane(2)-heptane(3)	0.346	0.330	343.7	36762.7	106.9	0.3	3.6
18	Water(1)-nitromethane(2)1-octene(3)	0.423	0.367	350.5	38695.9	110.4	2.3	0.3
19	Water(1)-nitromethane(2)-octane(3)	0.438	0.371	350.8	38895.8	110.8	2.5	0.8
20	Water(1)-nitromethane(2)-1-nonene(3)	0.530	0.388	354.2	40024.5	112.9	2.1	4.0
21	Water(1)-nitromethane(2)-nonane(3)	0.494	0.419	353.8	40040.3	113.1	2.9	3.9
22	Water(1)-nitromethane(2)-1-decene(3)	0.609	0.356	355.6	40723.8	114.5	1.6	6.4
23	Water(1)-nitromethane(2)-decane(3)	0.524	0.438	355.6	40254.6	113.2	1.6	4.5
24	Water(1)-nitromethane(2)-undecane(3)	0.480	0.504	355.9	39975.6	112.3	0.9	3.6
25	Water(1)-nitromethane(2)-dodecane(3)	0.488	0.504	356.3	39866.3	111.9	0.1	3.3
26	Water(1)-trichloro ethylene(2)-acetonitrile(3)	0.252	0.394	340.1	35821.5	105.3	1.3	5.8
27	Water(1)-trichloro ethylene(2)-isopropyl alcohol(3)	0.304	0.435	342.5	37787.6	110.3	7.5	1.2
28	Water(1)-trichloro ethylene(2)-propyl alcohol(3)	0.323	0.512	344.7	37227.3	108.0	5.9	3.6
29	Water(1)-acetonitrile(2)-benzene(3)	0.240	0.299	339.1	35107.5	103.5	4.3	6.6
30	Water(1)-acetonitrile(2)-triethylamine(3)	0.151	0.182	341.7	34452.7	100.8	2.1	11
31	Water(1)-1,2 dichloeroethane(2)-ethanol(3)	0.263	0.513	340.9	38296.2	112.3	7.3	1.4
32	Water(1)-1,2 dichloeroethane(2)-isopropyl alcohol(3)	0.288	0.499	342.8	37742.5	110.1	5.3	0.9
33	Water(1)-acetonitrile(2)-ethanol(3)	0.024	0.462	346.0	38682.1	111.7	1.1	2.6
34	Water(1)-ethanol(2)-acrylonitrile(3)	0.214	0.195	342.6	37046.6	108.1	2.1	1.2
35	Water(1)-ethanol(2)-ethyl acrylate(3)	0.277	0.518	350.2	39262.8	112.1	3.0	2.3
36	Water(1)-ethanol(2)-chlorobenzene(3)	0.168	0.777	350.4	41407.5	118.1	8.0	8.8
37	Water(1)-ethanol(2)-benzene(3)	0.233	0.228	338.0	36847.4	109.0	2.2	1.3
38	Water(1)-ethanol(2)-cyclohexane(3)	0.167	0.269	335.7	36426.1	108.5	3.1	2.2
39	Water(1)-ethanol(2)-hexane(3)	0.112	0.274	329.5	34658.3	105.2	0.9	5.6
40	Water(1)-ethanol(2)-triethylamine(3)	0.322	0.182	347.8	36272.7	104.3	1.3	6.6
41	Water(1)-ethanol(2)-toluene(3)	0.329	0.397	347.5	40819.6	117.4	8.5	7.6
42	Water(1)-ethanol(2)-heptane(3)	0.204	0.431	341.9	39059.9	114.2	8.0	3.6
43	Water(1)-isopropyl alcohol(2)2-butanone(3)	0.330	0.009	346.5	35120.3	101.3	6.4	8.9
44	Water(1)-isopropyl alcohol(2)-benzene(3)	0.249	0.186	339.6	36265.6	106.7	0.5	3.8
45	Water(1)-isopropyl alcohol(2)-cyclohexane(3)	0.260	0.192	337.4	35950.0	106.5	0.9	4.2
46	Water(1)-isopropyl alcohol(2)-toluene(3)	0.384	0.336	349.4	40040.1	114.5	6.4	4.5
47	Water(1)-propyl alcohol(2)-benzene(3)	0.257	0.102	340.1	35513.4	104.4	1.6	6.2
48	Water(1)-propyl alcohol(2)-cyclohexane(3)	0.294	0.104	339.7	35142.8	103.4	2.2	7.3
49	Water(1)-2-butanone(2)-benzene(3)	0.294	0.145	342.0	34580.3	101.1	5.2	9.5
50	Water(1)-2-butanone(2)-cyclohexane(3)	0.188	0.329	336.7	33917.0	100.7	3.8	10.0
51	Water(1)-butanol(2)-benzene(3)	0.327	0.012	342.1	34829.5	101.8	4.8	8.7
52	Water(1)-butanol(2)-butylacetate(3)	0.755	0.135	362.5	41103.9	113.3	0.1	6.0

Table 2 (*Continued*)

	System	x_1	x_2	T_b (K)	ΔH_v (J mol^{-1})	ΔS_v (J mol^{-1} K^{-1})	Eq. (9) (D_1)	Eq. (6) (D_2)
53	Water(1)-butanol(2)-hexane(3)	0.531	0.019	334.6	33953.3	101.4	6.9	8.3
54	Water(1)-butanol(2)-heptane(3)	0.790	0.035	351.2	38616.1	109.9	3.9	2.2
55	Water(1)-butanol(2)-octane(3)	0.888	0.053	359.2	41453.5	115.4	2.0	10.0
56	Water(1)-butanol(2)-nonane(3)	0.920	0.059	363.1	42494.8	117.0	2.0	14.0
57	Water(1)-tert-butanol(2)-benzene(3)	0.274	0.176	340.4	35707.1	104.9	1.1	5.8
58	Water(1)-tert-butanol(2)-cyclohexane(3)	0.283	0.180	338.1	35397.7	104.7	0.7	6.1
59	Water(1)-isobutanol(2)-toluene(3)	0.515	0.115	354.4	39412.8	111.2	2.6	1.3
60	Water(1)-pyridine(2)-octane(3)	0.616	0.159	359.8	39223.5	109.0	0.4	0.4
61	Water(1)-pyridine(2)-nonane(3)	0.757	0.158	363.6	41254.5	113.4	0.1	6.0
62	Water(1)-pyridine(2)-decane(3)	0.735	0.215	365.4	41673.9	114.0	0.8	6.7
63	Chloroform(1)-methanol(2)-acetone(3)	0.239	0.446	330.6	35291.9	106.7	1.1	3.7
64	Chloroform(1)-methanol(2)-methyl acetate(3)	0.300	0.461	329.5	35569.3	107.9	3.8	2.8
65	Chloroform(1)-ethanol(2)-acetone(3)	0.459	0.190	341.3	33191.8	97.2	4.6	14.0
66	Chloroform(1)-ethanol(2)-hexane(3)	0.437	0.192	330.4	33210.3	100.5	0.4	11.0
67	Methanol(1)-acetone(2)-cyclohexane(3)	0.289	0.433	324.2	35004.3	107.9	1.9	2.0
68	Methanol(1)-methyl acetate(2)-cyclohexane(3)	0.345	0.407	323.9	35564.2	109.7	4.6	0.4
69	Acetic acid(1)-pyridine(2)-ethybenzene(3)	0.201	0.284	402.2	38399.0	95.4	7.7	13.0
70	Acetic acid(1)-pyridine(2)-*o*-xylene(3)	0.252	0.330	405.3	38605.1	95.2	8.6	12.7
71	Acetic acid(1)-pyridine(2)-*p*-xylene(3)	0.156	0.261	402.3	38265.1	95.1	7.7	13.7
72	Acetic acid(1)-pyridine(2)-octane(3)	0.167	0.245	388.8	37533.9	96.5	5.2	13.8
73	Acetic acid(1)-pyridine(2)-nonane(3)	0.312	0.336	401.1	39374.5	98.1	4.8	10.6
74	Acetic acid(1)-pyridine(2)-decane(3)	0.429	0.396	407.2	39839.7	97.8	6.6	9.9
75	Acetic acid(1)-benzene(2)-cyclohexane(3)	0.101	0.351	350.3	34649.3	98.8	4.0	13.0
76	Isopropyl alcohol(1)-2-butanone(2)-cyclohexane(3)	0.291	0.174	342.0	35726.4	104.4	1.1	6.9
77	Isopropyl alcohol(1)-benzene(2)-cyclohexane(3)	0.383	0.142	342.2	36494.6	106.6	3.1	4.7
78	Butanol(1)-pyridine(2)-toluene(3)	0.139	0.227	381.8	36947.9	96.7	6.1	14.0
						106.2[a]	3.5[b]	6.6[b]

[a] Average value: $\Delta S_{v,av}$.

[b] Average deviation ($(1/n)\sum_{j=1}^{n} D_j$); $D_1 = |\Delta S_v - \Delta S_v \text{ (Eq. 9)}|$; $D_2 = |\Delta S_v - \Delta S_v \text{ (Eq.(6))}|$; n: number of systems.

from predictions. The average deviations for the binary azeotropes were found to be 4.6% from Eq. (8) and 7.6% from Eq. (6), while they are 3.5% from Eq. (9) and 6.6% from Eq. (6) for the ternary azeotropes. The proposed correlation expressions (8) and (9) yield satisfactory predictions for the entropy of vaporization of the azeotropes at the normal boiling point compared with those given by Eq. (6). The average values of the entropy of vaporization, $\Delta S_{v,av}$ are 105.3 J mol^{-1} K^{-1} for 97 binary azeotropes producing a standard deviation, SD of 6.1%, and 106.2 J mol^{-1} K^{-1} for 78 ternary azeotropes with a standard deviation of 6.4%

$$\mathrm{SD} = \left[\frac{1}{n-1}\sum_{i=1}^{n}(\Delta S_v - \Delta S_{v,av})^2\right]^{1/2} \qquad (10)$$

where n is the number of systems.

As seen from Table 1, the binary systems of 9 to 19 containing water(1)-hydrocarbon have the values of ΔS_v that increase gradually as the number of carbon atom increases. We see the similar behavior for the ternary systems of 14 to 25 and 53 to 56, shown in Table 2. This behavior is also the case for pure hydrocarbons [10].

As Table 2 shows that the ternary systems of 69 to 75 containing acetic acid and hydrocarbons have lower values of ΔS_v than that of the value of $\Delta S_{v,av}$, and yield higher absolute deviations. This is not so for the binary azeotropes of the systems 55 to 62, containing acetic acid, as shown in Table 1. If we exclude the ternary systems of 69 to 75, then the average deviation decreases to 3.1% from 3.5%, and the average value of ΔS_v increases to 107.2 from 106.2 J mol^{-1} K^{-1}, the value of SD decreases to 5.6 from 6.1%, while Eq. (9)

becomes

$$\Delta S_v = 86.812 + 11.552 \ln\left(\frac{T_b}{M_{av}}\right) \text{ for 71 ternary azeotropes without acetic acid} \quad (11)$$

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