Excess Volumes of Ternary Mixtures

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An expression for excess volumes of multi-component mixtures was derived, and its applicability to the experimental values of ternary mixtures was demonstrated. It was found, in 1,2-dichloroethane+benzene+cyclohexane, ethanol+benzene+cyclohexane and ethanol+acetone+cyclohexane mixtures, that the agreements between the calculated and the experimental values were satisfactory.

Many expressions and models for the thermodynamic properties of a liquid mixture have been proposed by many workers in the past two decades. Of these theories, some semi-empirical equations, such as the Wilson equation[1,2] and the UNIFAC equation,[3] have successfully interpreted the experimental values in many liquid mixtures. These theories can be extended to the calculation of the thermodynamic quantities observed in the multi-component mixtures,[1-4] despite some ambiguity in the physical meaning of the parameters involved. However, these theories are useless for the expression of the excess volume of the mixtures.

From this point of view, the present author recently proposed a new semi-empirical expression for the excess volume of binary mixtures based on the local composition in the mixture, and demonstrated that the results calculated by means of the equation are in good agreement with the experimental values.[5] This expression contains only two semi-empirical parameters for molecular arrangement in a binary mixture and can be expected to be extended to ternary mixtures in a simple manner. In this study, the expression for multi-component mixtures was derived, after which we examined its applicability to the experimental values obtained in three different ternary mixtures, 1,2-dichloroethane+benzene+cyclohexane, ethanol+benzene+cyclohexane, and ethanol+acetone+cyclohexane mixtures, selected as typical mixtures.

Theoretical

In multi-component mixtures consisting of n species, consider the n kinds of cells, each of them including an i-th ($1 \leqq i \leqq n$) component at the center. In this situation, if molecular association can be neglected, the volume occupied by one mol of the central molecule i, v_i, is expressed as follows:[5]

$$v_i = v_{1i}x_{1i} + v_{2i}x_{2i} + \cdots + v_{ii}x_{ii} + \cdots + v_{ni}x_{ni}, \quad (1)$$

where v_{ji} is the volume of the i-th component surrounded by the j-th component, and where x_{ji} denotes a local mole fraction of the j-th component in the vicinity of the i-th component. From Eq. 1, the volume of the mixture, v_{mix}, is represented as follows:

$$v_{mix} = \sum_{i=1}^{n} x_i \left(\sum_{j=1}^{n} v_{ji}x_{ji} \right). \quad (2)$$

Since the volume of an ideal mixture, v_{ideal}, is:

$$v_{ideal} = \sum_{i=1}^{n} x_i v_i^* = \sum_{i=1}^{n} x_i v_{ii}, \quad (3)$$

where v_i^* denotes the molar volume of the pure i-th component, the excess volume, v^E, is represented as follows:

$$v^E = \sum_{i=1}^{n} x_i \left(\sum_{j=1}^{n} (v_{ji} - v_{ii})x_{ji} \right). \quad (4)$$

In Eq. 4, the $\sum_{j=1}^{n} x_{ji} = 1$ relation was used. If the non-randomness factor, Λ_{ji}, is defined as:[5]

$$\frac{x_{ji}}{x_{ii}} = \Lambda_{ji}\frac{x_j}{x_i}, \quad (5)$$

the local mole fraction, x_{ji}, is represented as follows:

$$x_{ji} = \frac{\Lambda_{ji}x_j}{\sum_{k=1}^{n} \Lambda_{ki}x_k}. \quad (6)$$

From Eqs. 4 and 6, the expression for the excess volume of a multi-component mixture is obtained as follows:

$$v^E = \sum_{i=1}^{n} x_i \left(\frac{\sum_{j=1}^{n} (v_{ji} - v_{ii})\Lambda_{ji}x_j}{\sum_{k=1}^{n} \Lambda_{ki}x_k} \right). \quad (7)$$

The parameters $(v_{ji} - v_{ii})$ and Λ_{ji} can be obtained from the data of binary mixtures by a method previously described.[5]

Experimental

1,2-Dichloroethane, benzene, cyclohexane, acetone (Wako Pure Chemical Industries, Ltd.; G.R. grade) and ethanol (Kanto Chemical Co., Ltd.; G.R. grade) were used. Each of them was purified by means of fractional distillation on an apparatus with a 1.5-meter condenser under a reflux ratio of 3:1; a middle portion was collected at a constant condensation temperature. The purified reagents showed no signal due to any impurity on G.L.C. The densities and vapor pressures at 298.15 K agree well with the literature values.[6]

The excess volumes were obtained from density measurements made by using pycnometers with contents of 1.9 cm^3, 6 cm^3, and 9 cm^3 and immersed in a thermostat controlled at (298.15±0.001) K.

Results and Discussion

In this study, the excess volumes of binary and ternary mixtures were measured since only a few literature data on the excess volume of a ternary mixture are available.[7,8] The applicability of Eq. 7 was examined in the following sequence.

Binary Mixtures. The observed excess volumes of seven binary mixtures, *i.e.*, 1,2-dichloroethane+benzene, benzene+cyclohexane, 1,2-dichloroethane+cyclohexane, acetone+cyclohexane, ethanol+acetone,

TABLE 1. EXCESS VOLUMES v^E OF SEVEN BINARY MIXTURES AT 298.15K

x_1	v^E / cm^3 mol^{-1}	x_1	v^E / cm^3 mol^{-1}	x_1	v^E / cm^3 mol^{-1}
1,2-Dichloroethane(1) + benzene(2)		Benzene(1) + cyclohexane(2)		1,2-Dichloroethane(1) + cyclohexane(2)	
0.07120	0.1081	0.06079	0.2003	0.06588	0.3372
0.10135	0.1200	0.14356	0.3722	0.06958	0.3779
0.14697	0.1557	0.18165	0.4524	0.10138	0.5191
0.19028	0.1731	0.23076	0.5185	0.15762	0.6811
0.22435	0.2030	0.24060	0.5170	0.15879	0.6831
0.28366	0.2237	0.29127	0.6260	0.23505	0.8846
0.33058	0.2471	0.29313	0.5932	0.23586	0.8909
0.35393	0.2507	0.38093	0.7011	0.31166	0.9980
0.38791	0.2502	0.38643	0.7074	0.36840	1.0745
0.47153	0.2621	0.41625	0.7250	0.46430	1.0739
0.47828	0.2372	0.45588	0.6971	0.47928	1.0876
0.56491	0.2381	0.51291	0.7114	0.53750	1.0431
0.58035	0.2455	0.57722	0.7064	0.56165	1.0224
0.64277	0.2202	0.59442	0.6634	0.64041	0.8872
0.67581	0.2077	0.65144	0.6471	0.65305	0.8999
0.74666	0.1863	0.68664	0.6241	0.70900	0.8054
0.76017	0.1795	0.74889	0.5246	0.81384	0.5500
0.86542	0.1036	0.76753	0.5040	0.82661	0.5389
0.86850	0.0978	0.77438	0.4857	0.83954	0.5059
0.93796	0.0504	0.85142	0.3645	0.92938	0.2338
0.94712	0.0416	0.85738	0.3682	0.93417	0.2255
		0.92058	0.2318		
		0.94684	0.1672		
Acetone(1) + cyclohexane(2)		Ethanol(1) + benzene(2)		Ethanol(1) + cyclohexane(2)	
0.06944	0.3595	0.03181	0.0472	0.03778	0.1260
0.17215	0.7183	0.04746	0.0671	0.08566	0.2393
0.25602	0.9083	0.09497	0.0930	0.09387	0.2511
0.39779	1.0857	0.13980	0.0923	0.15896	0.3434
0.51404	1.1271	0.20116	0.0937	0.19412	0.3902
0.61379	1.0716	0.26573	0.0775	0.23602	0.4386
0.70018	0.9549	0.27633	0.0848	0.33095	0.5085
0.80288	0.7337	0.31006	0.0808	0.40925	0.5383
0.88628	0.4648	0.40830	0.0610	0.49511	0.5540
0.95246	0.2142	0.50169	0.0366	0.55255	0.5432
		0.55738	0.0126	0.60901	0.5317
Ethanol(1) + acetone(2)		0.63807	−0.0055	0.68480	0.5153
0.05530	−0.0064	0.66235	−0.0040	0.74540	0.4709
0.15373	−0.0236	0.72272	−0.0225	0.81722	0.3989
0.30963	−0.0411	0.77333	−0.0334	0.87048	0.3124
0.40671	−0.0548	0.82111	−0.0352	0.92440	0.2034
0.50854	−0.0587	0.86939	−0.0318	0.97483	0.0778
0.57634	−0.0702	0.92857	−0.0198		
0.59389	−0.0622	0.95126	−0.0179		
0.70507	−0.0614				
0.80208	−0.0562				
0.90075	−0.0331				
0.94251	−0.0249				

ethanol+benzene, and ethanol+cyclohexane mixtures, are listed in Table 1. These mixtures were selected because they are strongly non-ideal mixtures and because they possess a sufficient magnitude of excess volumes to be measured from density with sufficient accuracy. The data obtained were smoothed by the method of least squares to the following polynomial equation:

$$v^E = x(1-x)\sum_{i=0}^{4} A_i\,(1-2x)^i. \qquad (8)$$

TABLE 2. THE VALUES OF COEFFICIENTS FOR THE POLYNOMIAL EQUATION (Eq. 8) AT 298.15K

Mixtures	A_0	A_1	A_2	A_3	A_4	$\sigma(v^E)$ / cm^3 mol^{-1}
1,2-Dichloroethane(1)+benzene(2)	1.0077	0.1291	0.1322	0.2546	0.0560	0.0072
Benzene(1)+cyclohexane(2)	2.8772	0.1674	−0.2828	−0.1473	1.0377	0.0158
1,2-Dichloroethane(1)+cyclohexane(2)	4.2462	1.1368	0.1794	−0.0789	0.5340	0.0175
Acetone(1)+cyclohexane(2)	4.5015	0.0283	0.6692	0.6683	0.2233	0.0023
Ethanol(1)+acetone(2)	−0.2438	0.1250	−0.0341	0.0354	−0.0281	0.0026
Ethanol(1)+benzene(2)	0.1431	0.4873	−0.1413	0.5359	0.7410	0.0043
Ethanol(1)+cyclohexane(2)	2.2039	−0.1407	0.8225	0.2304	0.4036	0.0120

The obtained parameters, A_i, and standard deviation, σ, are summarized in Table 2. The partial molar volumes at an infinite dilution, v_i^∞ (as $v_i^\infty - v_i^*$), non-randomness factors, Λ_{ji}, and volume parameters, $v_{ji}-v_{ii}$ are also listed in Table 3. The volume parameters were calculated from $v_i^\infty - v_i^*$ by the use of the following equation:

$$v_{ji} - v_{ii} = \frac{(v_i^\infty - v_i^*) - \Lambda_{ij}(v_j^\infty - v_j^*)}{1 - \Lambda_{ij}\Lambda_{ji}}. \quad (9)$$

From Eq. 9, the volume change in the central molecule, i, surrounded by an unlike molecule, j, can be estimated. In the mixtures which show a positive deviation, the $v_{21}-v_{11}$ and $v_{12}-v_{22}$ values are smaller than the values of the corresponding $v_1^\infty - v_1^*$ and $v_2^\infty - v_2^*$ respectively. The $v_i^\infty - v_i^*$ values contain the volume changes of both the central and the surrounding molecules. On the other hand, the $v_{ij}-v_{jj}$ values consist of only the volume change of the central molecule. In the ethanol+acetone mixture, which shows a negative excess volume, the small $v_{12}-v_{22}$ value of acetone shows little volume change upon interaction with ethanol molecules, while the negative value of $v_{21}-v_{11}$ for ethanol shows a decrease in the volume upon interaction with acetone. In the ethanol+benzene mixture, the negative value of the volume change of benzene indicates the OH-π interaction and the positive value of ethanol molecule results from the destruction of the hydrogen-bonding interaction of the ethanol molecules.

The excess volumes calculated from Eq. 7 are in good agreement with the experimental values, shown by solid lines in Fig. 1. The solid lines were drawn on the basis of Eq. 7.

Ternary Mixtures. The excess volumes of three ternary mixtures, the 1,2-dichloroethane+benzene+cyclohexane, ethanol+benzene+cyclohexane, and ethanol+acetone+cyclohexane mixtures, were measured and compared with the values calculated from Eq. 7. In the 1,2-dichloroethane+benzene+cyclohexane mixture, all binary mixtures composed of the three components show positive excess volumes. In the ethanol+benzene+cyclohexane mixture, the ethanol+benzene binary mixture shows an S-shaped excess-volume curve. The ethanol+acetone mixture in the ethanol+acetone+cyclohexane mixture shows a negative excess volume. These three ternary mixtures are typical systems which show representative excess-volume curves. When two binary mixtures composed of the components of the ternary mixtures show negative excess volumes, the calculated and observed excess volumes are considered to have a tendency similar to that when two binary mixtures show positive excess volumes, if the signs of the values of the excess volume and the volume parameters are changed.

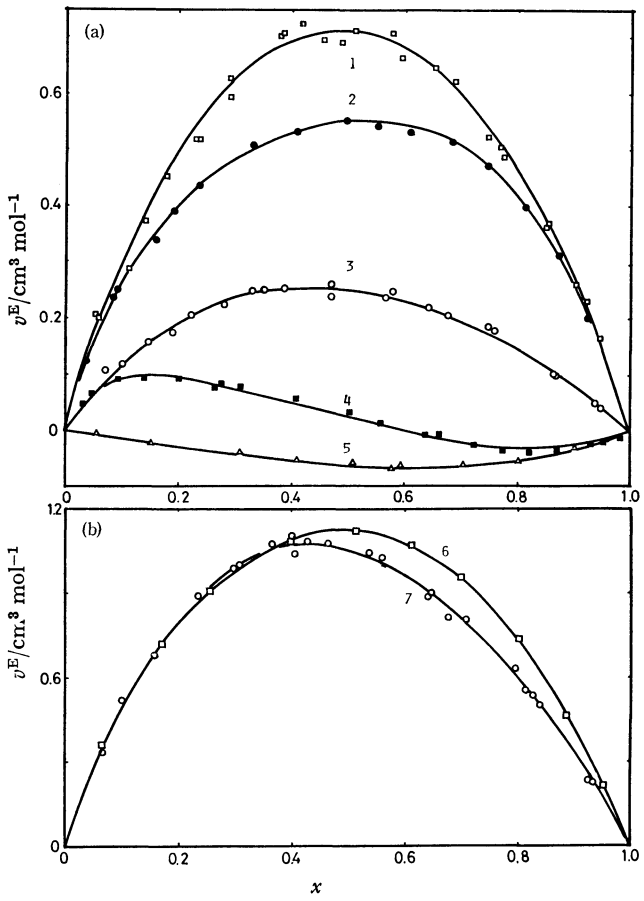

Fig. 1. Observed and calculated excess volumes of seven binary mixtures at 298.15 K.
The solid lines indicate the calculated curves from Eq. 7 using the values of parameters in Table 3. 1; Benzene+cyclohexane, 2; ethanol+cyclohexane, 3; 1,2-dichloroethane+benzene, 4; ethanol+benzene, 5; ethanol+acetone mixtures, which are shown in Fig. 1a, and 6, acetone+cyclohexane; 7, 1,2-dichloroethane+cyclohexane mixtures are shown in Fig. 1(b).

The observed and calculated excess volumes of the

TABLE 3. THE DERIVED QUANTITIES FROM THE COEFFICIENTS A_i IN Eq. 8 AND THE APPLICABILITY OF Eq. 7

Mixtures	$v_1^\infty - v_1^*$ / cm³ mol⁻¹	$v_2^\infty - v_2^*$ / cm³ mol⁻¹	A_{21}	A_{12}	$v_{21} - v_{11}$ / cm³ mol⁻¹	$v_{12} - v_{22}$ / cm³ mol⁻¹	$\sigma(v^E)$ / cm³ mol⁻¹
1,2-Dichloroethane(1) + benzene(2)	1.5795	0.8122	0.4786[a)]	0.1812[a)]	1.4385	0.2233	0.0096
Benzene(1) + cyclohexane(2)	3.6522	3.6121	3.7543	2.4504	0.6342	1.2317	0.0231
1,2-Dichloroethane(1) + cyclohexane(2)	6.0775	3.9617	6.3452	2.0276	0.1648	2.9161	0.0192
Acetone(1) + cyclohexane(2)	6.0906	4.6973	0.1406	0.8253	2.5045	4.3452	0.0089
Ethanol(1) + acetone(2)	−0.1457	−0.4664	2.7140	3.0170	−0.1755	0.0099	0.0026
Ethanol(1) + benzene(2)	1.7661	−0.2803	0.1594	0.7006	2.2092	−0.6325	0.0125
Ethanol(1) + cyclohexane(2)	3.5196	3.3403	0.1991	0.3125	2.6404	2.8150	0.0064

a) Calculated from the following values of the coefficients in Eq. 8; $A_0=0.9918$, $A_1=0.2836$, and $A_2=0.2036$.

TABLE 4. OBSERVED EXCESS VOLUMES, v^E_{obsd}, OF TERNARY MIXTURES AT 298.15K, AND THE CALCULATED VALUES, v^E_{calcd}, FROM Eq. 7

x_1	x_2	v^E_{obsd} / cm³ mol⁻¹	v^E_{calcd} / cm³ mol⁻¹	x_1	x_2	v^E_{obsd} / cm³ mol⁻¹	v^E_{calcd} / cm³ mol⁻¹
1,2-Dichloroethane(1) + benzene(2) + cyclohexane(3)							
0.16181	0.10822	0.8315	0.8015	0.37619	0.54744	0.4351	0.4083
0.15592	0.21786	0.8157	0.8252	0.45702	0.09156	1.0273	0.9653
0.14390	0.37338	0.8273	0.7925	0.43892	0.18588	0.9461	0.8673
0.13755	0.47434	0.7918	0.7373	0.41082	0.31482	0.8013	0.7319
0.13277	0.56359	0.7193	0.6641	0.56022	0.08152	0.9615	0.8833
0.11488	0.80393	0.3625	0.3235	0.55097	0.17551	0.8206	0.7543
0.29002	0.09498	0.9836	0.9628	0.50679	0.29440	0.6726	0.6339
0.27667	0.21334	0.9823	0.9016	0.56591	0.36310	0.4285	0.3989
0.25582	0.34827	0.8407	0.8075	0.66078	0.07835	0.7828	0.7378
0.24893	0.45729	0.7750	0.7051	0.63407	0.16175	0.6916	0.6407
0.24202	0.62002	0.4896	0.4873	0.65913	0.27086	0.4052	0.3784
0.22318	0.69970	0.3564	0.3686	0.71173	0.15909	0.5088	0.4862
0.38916	0.40256	0.7039	0.6344	0.82163	0.06866	0.4246	0.4038
0.38602	0.47876	0.5567	0.5174	0.86941	0.06419	0.2869	0.2794
Ethanol(1) + acetone(2) + cyclohexane(3)							
0.13745	0.12130	0.6836	0.5907	0.47672	0.13572	0.6534	0.6261
0.14842	0.25582	0.9083	0.8309	0.45854	0.35078	0.5087	0.5031
0.14338	0.41722	0.9673	0.9366	0.47704	0.44319	0.2248	0.2319
0.13677	0.57478	0.8414	0.8307	0.53882	0.10430	0.6109	0.5868
0.12985	0.75011	0.4483	0.4442	0.52280	0.23803	0.5571	0.5427
0.25102	0.39847	0.8991	0.8054	0.54100	0.38390	0.1779	0.2076
0.39128	0.06770	0.6438	0.5968	0.65937	0.16991	0.4060	0.4041
0.36529	0.30142	0.7405	0.7073	0.81402	0.08978	0.2365	0.2432
0.38048	0.43502	0.5380	0.5222				
Ethanol(1) + benzene(2) + cyclohexane(3)							
0.14628	0.14040	0.5768	0.6360	0.42111	0.20990	0.6265	0.6558
0.15294	0.31744	0.7299	0.7773	0.40934	0.32452	0.5651	0.5935
0.13411	0.42651	0.7239	0.7751	0.44806	0.39016	0.4087	0.4415
0.14881	0.55405	0.6448	0.6919	0.46057	0.45622	0.2535	0.2790
0.12821	0.57810	0.6308	0.6861	0.54359	0.09818	0.5727	0.5864
0.14142	0.77175	0.3020	0.3576	0.57801	0.28090	0.3356	0.3617
0.25864	0.45372	0.6269	0.6685	0.62485	0.13932	0.4693	0.4793
0.39986	0.33098	0.5707	0.6003	0.80450	0.05251	0.3209	0.3258
0.45345	0.07094	0.5974	0.6222	0.84905	0.11362	0.0792	0.0895

ternary mixtures are summarized in Table 4. As is shown in this table, the calculated excess volumes of all the ternary mixtures are in good agreement with the experimental values. The maximum difference between the calculated and the observed values is about 0.09 $cm^3\ mol^{-1}$, most of the differences are within 0.05 $cm^3\ mol^{-1}$.

As has been described above, the present expression for the excess volumes of multi-component mixtures is considered to be successful in reproducing the experimental values. As Eq. 7 shows, the excess volume can be determined in terms of the molecular arrangement in a mixture, the intermolecular interaction assessed by non-randomness factors, and the molecular size as measured from the $v_{ij}-v_{jj}$ values.

From these results and this discussion, it should be noticed that the excess volumes of ternary mixtures can be represented without ternary terms of molecular-size parameters and three-body interaction in a given mixture, as was shown in the derivation of Eq. 7. The effect of three-body interaction is considered to be small, and the degree of correction required for the three-body terms can be assumed to be of the same magnitude as the difference between the observed and the calculated values in Table 4, *i.e.*, about 0.05 $cm^3\ mol^{-1}$.

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