Excess Volumes of Binary Solutions Containing Some Diketones

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As part of thermodynamic studies on binary solutions containing diketones, the excess volumes of the following four systems have been measured at 25.00°C. They are acetylacetone(2,4-pentanedione)-acetone, acetylacetone-isopropanol, acetonylacetone(2,5-hexanedione)-acetone, and acetonylacetone-isopropanol. Acetylacetone is one of those molecules which exhibit keto-enol tautomerism. It is frequently used as a substrate of metal complex in coordination chemistry. The purpose of this study is to examine a combined effect of size difference in polar molecules and keto-enol equilibrium on the thermodynamic excess functions, in this particular case, on the excess volume.

Experimental

All the sample liquids were purified by distillation under nitrogen atmosphere and/or at reduced pressure. The final purified liquids obtained from the middle fraction gave no peaks due to impurities on gas chromatogram. The density measurements were done by the pycnometry described in our previous report.[1]

Results and Discussion

The densities of the four systems studied are shown in Table 1. The excess volumes which were calculated from the density data are also given in the same table and are plotted as a function of mole fraction in Fig. 1. The excess volumes of acetone-isopropanol system, calculated from the density data given by Parks and Chaffee,[2] are also included. The solid lines in Fig. 1 are based on the values calculated by the following equation,

$$\Delta V^E = x_1(1-x_1)\sum_{n=0}^{2} A_n(1-2x_1)^n \qquad (1)$$

where the constants A_n's were estimated by the method of least-squares. The data for acetonylacetone-acetone system show fairly large scatter owing to a high relative volatility and viscous nature of one component. The results for other systems are satisfactory.

The results shown in Fig. 1 may be summarized as follows:

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1) K. Nakanishi, N. Kato and M. Maruyama, *J. Phys. Chem.*, **71**, 817 (1967).

2) G. S. Parks and C. S. Chaffee, *ibid.*, **31**, 439 (1927).

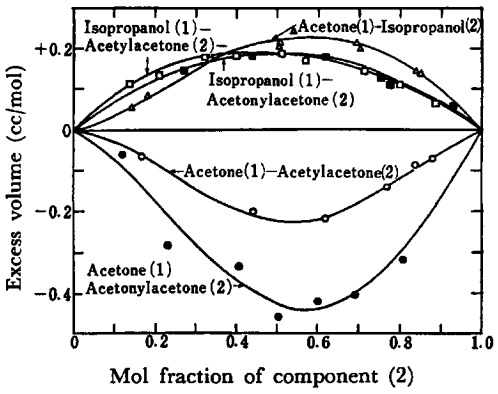

Fig. 1. Excess volumes at 25.00°C.

1) In binary systems containing isopropanol, the excess volumes are positive and their values coincide almost completely with each other.

2) Since the molar volume ratio of acetone, acetylacetone and acetonylacetone is 1.00 : 1.40 : 1.60, the first two can be regarded approximately as dimers of acetone molecule. The excess volumes of the systems containing acetone and diketones are negative and their absolute value increases with the molar volume difference.

Owing to the lack of adequate theory for such polar and associated solutions, quantitative evaluation of the present data is difficult. However, it is interesting to compare them with the results for mixtures of nonpolar molecules. For mixtures of nonpolar molecules, it is found by Brønsted and Koefoed[3] that the absolute value of the excess volume changes regularly with the size difference (principle of congruence). According to the available experimental evidences,[4-6] the magnitude of the excess volume is proportional to the size difference. On the other hand, the sign of the excess volume is dependent of the shape of molecules. For example, negative excess volume is observed for mixtures of molecules of similar shape such as *n*-alkane-*n*-alkane,[4] and an opposite result is obtained for mixtures of molecules of different shape (*e. g.*, cyclohexane-*n*-alkanes[5] or *trans*-decalin-*n*-alkane[6]).

Table 1. Density and excess volume at 25.00°C

Mole fraction of 1st component x_1	Density d (g/cc)	Excess volume ΔV^E (cc/mol)
Acetone (1)—Acetylacetone (2)		
0.0	0.96942	
0.1686	0.94710	−0.0649
0.4407	0.90527	−0.2001
0.6179	0.87303	−0.2198
0.6715	0.86233	−0.2109
0.7712	0.84076	−0.1405
0.8359	0.82585	−0.0875
0.8796	0.81559	−0.0719
1.0	0.78392	
Isopropanol (1)—Acetylacetone (2)		
0.1386	0.94810	+0.1148
0.2105	0.93679	+0.1372
0.3264	0.91752	+0.1839
0.3996	0.90500	+0.1834
0.5116	0.88477	+0.1865
0.5722	0.87344	+0.1703
0.7092	0.84611	+0.1467
0.7991	0.82706	+0.1123
0.8827	0.80850	+0.0626
1.0	0.78056	
Acetone (1)—Acetonylacetone (2)		
0.0	0.96758	
0.1201	0.95361	−0.0629
0.2310	0.94092	−0.2856
0.4049	0.90567	−0.3396
0.5025	0.90062	−0.4612
0.5989	0.88274	−0.4202
0.6623	0.86991	−0.3782
0.6891	0.86471	−0.4074
0.8071	0.83780	−0.3210
Isopropanol (1)—Acetonylacetone (2)		
0.2677	0.91413	+0.1502
0.4356	0.88785	+0.1838
0.6174	0.85673	+0.1826
0.7528	0.83181	+0.1291
0.7750	0.82753	+0.1130
0.9306	0.79566	+0.0613

The present data conform with such rules. We expected that there should be some unnegligible effect of the presence of keto-enol equilibrium on the excess function behavior. As far as the present data are concerned, no such effect was found.

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6) J. D. Gómez-Ibánez and T. C. Wang, *ibid.*, **70**, 391 (1966).